AUCHE 112 - GENERAL CHEMISTRY II



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AUCHE 112 - General Chemistry II

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TABLE OF CONTENTS

Licensing

1: Thermochemistry

- 1.1: The Nature of Energy
- 1.2: Energy Basics
- 1.3: Calorimetry
- 1.4: Enthalpy
- 1.5: Standard Thermodynamic Properties for Selected Substances
- 1.6: Bond Energies

2: Spontaneity, Entropy and Free Energy

- 2.1: Spontaneity
- 2.2: Entropy and the Second Law of Thermodynamics
- 2.3: The Molecular Interpretation of Entropy
- 2.4: Entropy Changes in Chemical Reactions
- 2.5: Gibbs Energy
- 2.6: Standard Thermodynamic Properties for Selected Substances

3: Reaction Kinetics

- 3.1: Chemical Reaction Rates
- 3.2: Factors Affecting Reaction Rates
- 3.3: Rate Laws
- 3.4: Integrated Rate Laws
- 3.5: First-Order Reactions
- 3.6: Second-Order Reactions
- 3.7: Zero-Order Reactions
- 3.8: Pseudo-1st-order reactions
- 3.9: Reaction Mechanisms
- 3.10: The Collision Theory
- 3.11: Arrhenius Equation
- 3.12: Kinetics of Catalysis

4: Chemical Equilibrium

- 4.1: Prelude to Equilibrium
- 4.2: Chemical Equilibria
- 4.3: Equilibrium Constants
- 4.4: Free Energy and the Equilibrium Constant
- 4.5: Equilibrium Calculations
- 4.6: Precipitation and Dissolution
- 4.7: Solubility Products
- 4.8: Shifting Equilibria - Le Chatelier's Principle

5: Acids and Bases

- 5.1: Acids and Bases - A Brief Review
- 5.2: Brønsted–Lowry Acids and Bases
- 5.3: Lewis Acids and Bases
- 5.4: The Autoionization of Water
- 5.5: The pH Scale
- 5.6: Strong Acids and Bases
- 5.7: Weak Acids
- 5.8: Ionization Constants of Weak Acids
- 5.9: Weak Bases
- 5.10: Ionization Constants of Weak Bases
- 5.11: Relationship Between Ka and Kb
- 5.12: Acid-Base Properties of Salt Solutions
- 5.13: The Common-Ion Effect
- 5.14: Buffered Solutions
- 5.15: Acid-Base Titrations

6: Electrochemistry

- 6.1: Oxidation States and Redox Reactions
- 6.2: Balanced Oxidation-Reduction Equations
- 6.3: Voltaic Cells
- 6.4: Cell Potential Under Standard Conditions
- 6.5: Standard Electrode (Half-Cell) Potentials
- 6.6: Gibbs Energy and Redox Reactions
- 6.7: Cell Potential Under Nonstandard Conditions
- 6.8: Corrosion
- 6.9: Electrolysis

Index

Glossary

Detailed Licensing

Detailed Licensing

Licensing

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CHAPTER OVERVIEW

1: Thermochemistry

1.1: The Nature of Energy
1.2: Energy Basics
1.3: Calorimetry
1.4: Enthalpy
1.5: Standard Thermodynamic Properties for Selected Substances
1.6: Bond Energies

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1.1: The Nature of Energy

What is Energy?

Energy is one of the most fundamental and universal concepts of physical science, but one that is remarkably difficult to define in a way that is meaningful to most people. This perhaps reflects the fact that energy is not a “thing” that exists by itself, but is rather an attribute of matter (and also of electromagnetic radiation) that can manifest itself in different ways. It can be observed and measured only indirectly through its effects on matter that acquires, loses, or possesses it.

The concept that we call energy was very slow to develop; it took more than a hundred years just to get people to agree on the definitions of many of the terms we use to describe energy and the interconversion between its various forms. But even now, most people have some difficulty in explaining what it is; somehow, the definition we all learned in elementary science ("the capacity to do work") seems less than adequate to convey its meaning.

Although the term "energy" was not used in science prior to 1802, it had long been suggested that certain properties related to the motions of objects exhibit an endurance which is incorporated into the modern concept of "conservation of energy". In the 17th Century, the great mathematician Gottfried Leibnitz (1646-1716) suggested the distinction between *vis viva* ("live force") and *vis mortua* ("dead force"), which later became known as kinetic energy (1829) and potential energy (1853).

Kinetic energy and potential energy

Whatever energy may be, there are basically two kinds.

Kinetic energy is associated with the **motion** of an object, and its direct consequences are part of everyone's daily experience; the faster the ball you catch in your hand, and the heavier it is, the more you feel it. Quantitatively, a body with a mass m and moving at a velocity v possesses the kinetic energy $mv^2/2$.

Example 1

A rifle shoots a 4.25 g bullet at a velocity of 965 m s^{-1}. What is its kinetic energy?

Solution

The only additional information you need here is that

$$1\ J = 1\ kg\ m^2\ s^{-2}:$$

$$KE = ½ \times (.00425\ kg)\ (965\ m\ s^{-1})^2 = 1980\ J$$

Potential energy is energy a body has by virtue of its *location*. But there is more: the body must be subject to a "restoring force" of some kind that tends to move it to a location of lower potential energy. Think of an arrow that is subjected to the force from a stretched bowstring; the more tightly the arrow is pulled back against the string, the more potential energy it has.

More generally, the restoring force comes from what we call a *force field*— a gravitational, electrostatic, or magnetic field. We observe the consequences of *gravitational* potential energy all the time, such as when we walk, but seldom give it any thought.

If an object of mass m is raised off the floor to a height h, its potential energy increases by mgh, where g is a proportionality constant known as the *acceleration of gravity*; its value at the earth's surface is 9.8 m s^{-2}.

Example 2

Find the change in potential energy of a 2.6 kg textbook that falls from the 66-cm height of a table top onto the floor.

Solution

$$PE = m\,g\,h = (2.6\ kg)(9.8\ m\ s^{-2})(0.66\ m) = 16.8\ kg\ m^2\ s^{-2} = 16.8\ J$$

Similarly, the potential energy of a particle having an electric charge $q$depends on its location in an electrostatic field.

"Chemical energy"

Electrostatic potential energy plays a major role in chemistry; the potential energies of electrons in the force field created by atomic nuclei lie at the heart of the chemical behavior of atoms and molecules. "Chemical energy" usually refers to the energy that is

stored in the chemical bonds of molecules. These bonds form when electrons are able to respond to the force fields created by two or more atomic nuclei, so they can be regarded as manifestations of electrostatic potential energy. In an **exothermic** chemical reaction, the electrons and nuclei within the reactants undergo rearrangement into products possessing lower energies, and the difference is released to the environment in the form of heat.

Interconversion of potential and kinetic energy

Transitions between potential and kinetic energy are such an intimate part of our daily lives that we hardly give them a thought. It happens in walking as the body moves up and down. Our bodies utilize the chemical energy in glucose to keep us warm and to move our muscles. In fact, life itself depends on the conversion of chemical energy to other forms.

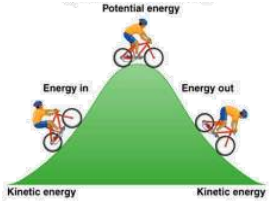


Figure: Conservation of energy applied to a bicyclist and a hill.

Energy is conserved: it can neither be created nor destroyed. So when you go uphill, your kinetic energy is transformed into potential energy, which gets changed back into kinetic energy as you coast down the other side. And where did the kinetic energy you expended in peddling uphill come from? By conversion of some of the chemical potential energy in your breakfast cereal.

- When drop a book, its potential energy is transformed into kinetic energy. When it strikes the floor, this transformation is complete. What happens to the energy then? The kinetic energy that at the moment of impact was formerly situated exclusively in the moving book, now becomes shared between the book and the floor, and in the form of randomized thermal motions of the molecular units of which they are made; we can observe this effect as a rise in temperature.
- Much of the potential energy of falling water can be captured by a water wheel or other device that transforms the kinetic energy of the exit water into kinetic energy. The output of a hydroelectric power is directly proportional to its height above the level of the generator turbines in the valley below. At this point, the kinetic energy of the exit water is transferred to that of the turbine, most of which (up to 90 percent in the largest installations) is then converted into electrical energy.
- Will the temperature of the water at the bottom of a water fall be greater than that at the top? James Joule himself predicted that it would be. It has been calculated that at Niagara falls, that complete conversion of the potential energy of 1 kg of water at the top into kinetic energy when it hits the plunge pool 58 meters below will result in a temperature increase of about 0.14 C°. (But there are lots of complications. For example, some of the water breaks up into tiny droplets as it falls, and water evaporates from droplets quite rapidly, producing a cooling effect.)
- Chemical energy can also be converted, at least partially, into electrical energy: this is what happens in a battery. If a highly exothermic reaction also produces gaseous products, the latter may expand so rapidly that the result is an explosion — a net conversion of chemical energy into kinetic energy (including sound).

Thermal energy

Kinetic energy is associated with motion, but in two different ways. For a macroscopic object such as a book or a ball, or a parcel of flowing water, it is simply given by $\frac{1}{2}mv^2$. However, as we mentioned above, when an object is dropped onto the floor, or when an exothermic chemical reaction heats surrounding matter, the kinetic energy gets dispersed into the molecular units in the environment. This "microscopic" form of kinetic energy, unlike that of a speeding bullet, is completely random in the kinds of motions it exhibits and in its direction. We refer to this as "thermalized" kinetic energy, or more commonly simply as *thermal energy*. We observe the effects of this as a rise in the temperature of the surroundings. The temperature of a body is direct measure of the quantity of thermal energy is contains.

Thermal energy is never completely recoverable

Once kinetic energy is thermalized, only a portion of it can be converted back into potential energy. The remainder simply gets dispersed and diluted into the environment, and is effectively lost.

To summarize, then:

- Potential energy can be converted entirely into kinetic energy..
- Potential energy can also be converted, with varying degrees of efficiency,into electrical energy.

- The kinetic energy of macroscopic objects can be transferred between objects (barring the effects of friction).
- Once kinetic energy becomes thermalized, only a portion of it can be converted back into either potential energy or be concentrated back into the kinetic energy of a macroscopic. This limitation, which has nothing to do with technology but is a fundamental property of nature, is the subject of the second law of thermodynamics.
- A device that is intended to accomplish the partial transformation of thermal energy into organized kinetic energy is known as a *heat engine*.

Energy scales are always arbitrary

You might at first think that a book sitting on the table has zero kinetic energy since it is not moving. But if you think about it, the earth itself is moving; it is spinning on its axis, it is orbiting the sun, and the sun itself is moving away from the other stars in the general expansion of the universe. Since these motions are normally of no interest to us, we are free to adopt an arbitrary scale in which the velocity of the book is measured with respect to the table; on this so-called *laboratory coordinate system*, the kinetic energy of the book can be considered zero.

We do the same thing with potential energy. If the book is on the table, its potential energy with respect to the surface of the table will be zero. If we adopt this as our zero of potential energy, and then push the book off the table, its potential energy will be negative after it reaches the floor.

Energy units

Energy is measured in terms of its ability to perform work or to transfer heat. Mechanical work is done when a force f displaces an object by a distance *d*:

$$w = f \times d \tag{1.1.1}$$

The basic unit of energy is the *joule*. One joule is the amount of work done when a force of 1 newton acts over a distance of 1 m; thus 1 J = 1 N-m. The newton is the amount of force required to accelerate a 1-kg mass by 1 m/sec^2, so the basic dimensions of the joule are kg m^2 s^{-2}. The other two units in wide use. the *calorie* and the *BTU* (British thermal unit) are defined in terms of the heating effect on water. Because of the many forms that energy can take, there are a correspondingly large number of units in which it can be expressed, a few of which are summarized below.

1 calorie will raise the temperature of 1 g of water by 1 C°. The "dietary" calorie is actually 1 kcal. An average young adult expends about 1800 kcal per day just to stay alive. (you should know this definition)	1 cal = 4.184 J
1 BTU (British Thermal Unit) will raise the temperature of 1 lb of water by 1F°.	1 BTU = 1055 J
The erg is the c.g.s. unit of energy and a very small one; the work done when a 1-dyne force acts over a distance of 1 cm.	1 J = 10^7 ergs 1 erg = 1 d-cm = 1 g cm^2 s^{-2}
The electron-volt is even tinier: 1 eV is the work required to move a unit electric charge (1 C) through a potential difference of 1 volt.	1 J = 6.24 × 1018 eV
The watt is a unit of power, which measures the rate of energy flow in J sec^{-1}. Thus the watt-hour is a unit of energy. An average human consumes energy at a rate of about 100 watts; the brain alone runs at about 5 watts.	1 J = 2.78 × 10^{-4}watt-hr 1 w-h = 3.6 kJ
The liter-atmosphere is a variant of force-displacement work associated with volume changes in gases.	1 L-atm = 101.325 J
The huge quantities of energy consumed by cities and countries are expressed in quads; the therm is a similar but smaller unit.	1 quad = 1015 Btu = 1.05 × 10^{18} J
If the object is to obliterate cities or countries with nuclear weapons, the energy unit of choice is the ton of TNT equivalent.	1 ton of TNT = 4.184 GJ (by definition)

In terms of fossil fuels, we have barrel-of-oil equivalent, cubic-meter-of-natural gas equivalent, and ton-of-coal equivalent.	1 bboe = 6.1 GJ 1 cmge = 37-39 mJ 1 toce = 29 GJ

Heat and Work

Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other, and from just plain “energy” itself? In our daily language, we often say that "this object contains a lot of heat", but this is gibberish in thermodynamics terms, although it is ok to say that the object is "hot", indicating that its temperature is high. The term "heat" has a special meaning in thermodynamics: it is a *process* in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings. Hence, thermal energy can only flow from a higher temperature to a lower temperature. It is this flow that constitutes "heat". Use of the term "flow" of heat recalls the incorrect 18th-century notion that heat is an actual substance called “caloric” that could flow like a liquid.

Note: Heat

We often say that "this object contains a lot of heat," however, this makes no sense since heat represents an energy transfer.

Transfer of thermal energy can be accomplished by bringing two bodies into physical contact (the kettle on top of the stove, or through an electric heating element inside the kettle). Another mechanism of thermal energy transfer is by radiation; a hot object will convey energy to any body in sight of it via electromagnetic radiation in the infrared part of the spectrum. In many cases, both modes will be active.

Work refers to the transfer of energy some means that does not depend on temperature difference. Work, like energy, can take various forms, the most familiar being mechanical and electrical.

- *Mechanical work* arises when an object moves a distance Δx against an opposing force f:

$$w = f\ \Delta x \tag{1.1.2}$$

- *Electrical work* is done when a body having a charge q moves through a potential difference ΔV.

Note: Work

A transfer of energy to or from a system by any means other than heat is called “work”.

Work can be completely converted into heat (by friction, for example), but heat can only be partially converted to work. **Conversion of heat into work** is accomplished by means of a *heat engine*, the most common example of which is an ordinary gasoline engine. The science of thermodynamics developed out of the need to understand the limitations of steam-driven heat engines at the beginning of the Industrial Age. The Second Law of Thermodynamics, states that the complete conversion of heat into work is impossible. Something to think about when you purchase fuel for your car!

Contributors and Attributions

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1.2: Energy Basics

Learning Objectives

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

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure **1.2.1**). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



(a) (b) (c)

Figure **1.2.1**: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner).

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

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

Energy

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

the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure **1.2.2**). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **1.2.2**: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Two pictures are shown and labeled a and b. Picture a shows a large waterfall with water falling from a high elevation at the top of the falls to a lower elevation. The second picture is a view looking down into the Hoover Dam. Water is shown behind the high wall of the dam on one side and at the base of the dam on the other.

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

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

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

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure **1.2.3**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

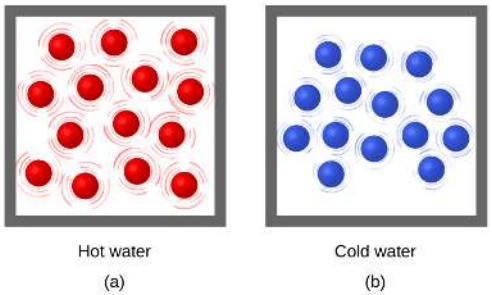
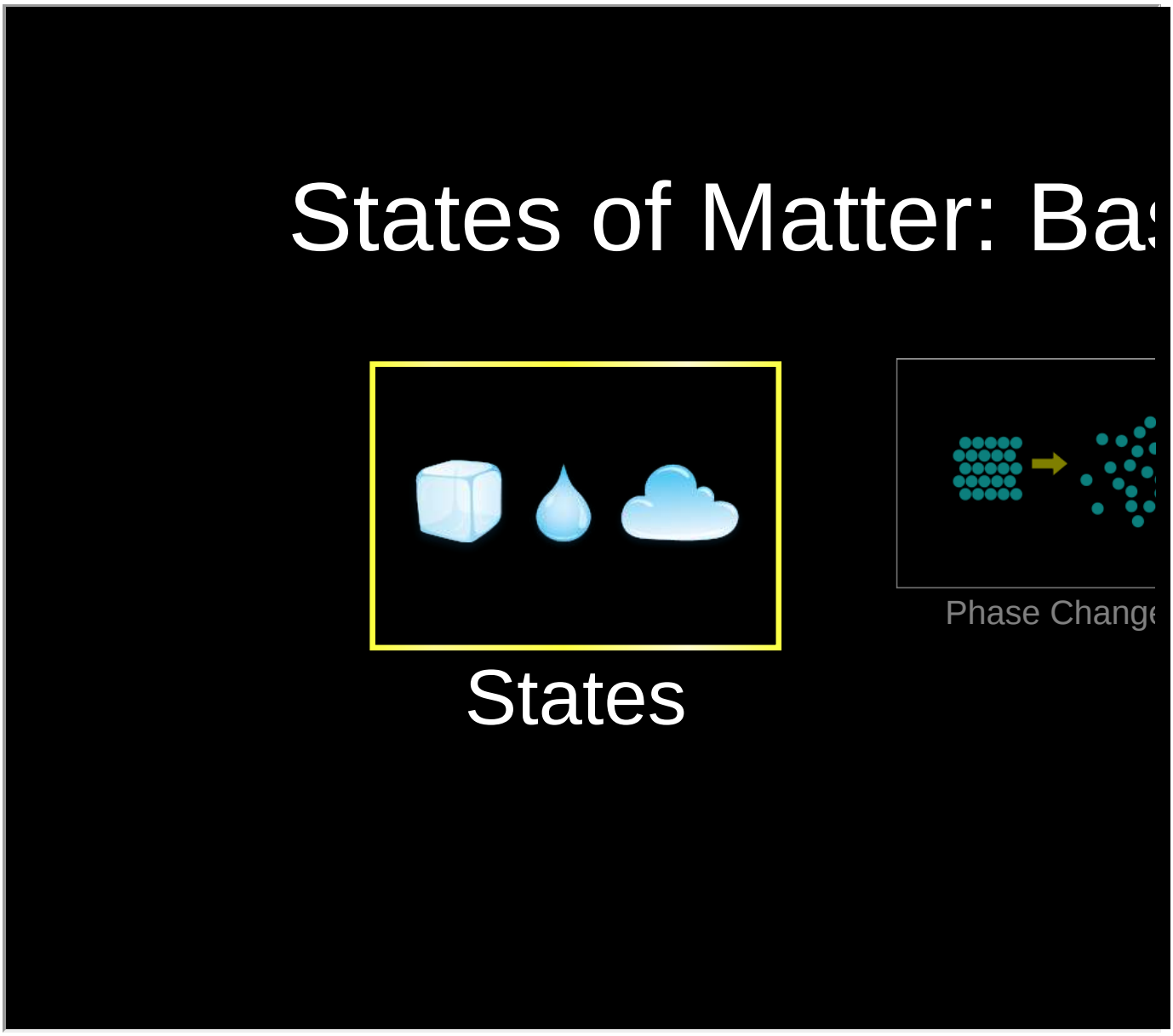


Figure **1.2.3**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Two molecular drawings are shown and labeled a and b. Drawing a is a box containing fourteen red spheres that are surrounded by lines indicating that the particles are moving rapidly. This drawing has a label that reads “Hot water.” Drawing b depicts another box of equal size that also contains fourteen spheres, but these are blue. They are all surrounded by smaller lines that depict some particle motion, but not as much as in drawing a. This drawing has a label that reads “Cold water.”



Measuring Energy and Heat Capacity

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

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

$$C = \frac{q}{\Delta T} \tag{1.2.1}$$

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

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

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ °C}} = 363 \text{ J/°C} \tag{1.2.2}$$

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

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ °C}} = 1814 \text{ J/°C} \tag{1.2.3}$$

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

$$c = \frac{q}{\text{m}\Delta\text{T}} \tag{1.2.4}$$

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

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{1.2.5}$$

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

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{1.2.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure **1.2.7**).



Figure **1.2.7**: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

The picture shows two black metal frying pans sitting on a flat surface. The left pan is about half the size of the right pan.

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table **1.2.1**.

Table **1.2.1**: Specific Heats of Common Substances at 25 °C and 1 bar

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

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

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

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

Example 1.2.1: Measuring Heat

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

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

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

This can be summarized using the equation:

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

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

Exercise 1.2.1

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

Answer

5.05×10^4 J

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

Example 1.2.2: Determining Other Quantities

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

Solution

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

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

Substituting the known values:

$$6,640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4) \text{ °C}$$

Solving:

$$c = \frac{6,640 \text{ J}}{(348 \text{ g}) \times (21.2 \text{°C})} = 0.900 \text{ J/g °C}$$

Comparing this value with the values in Table 1.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

? Exercise 1.2.2

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

Answer

$c = 0.45$ J/g °C; the metal is likely to be iron from checking Table 1.2.1.

Solar Thermal Energy Power Plants

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

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 1.2.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

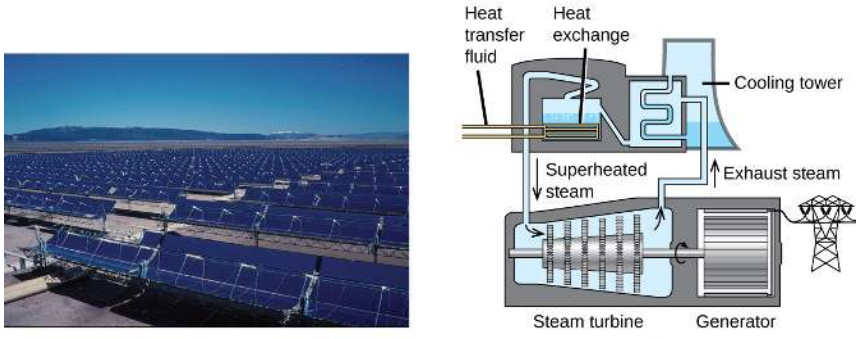


Figure 1.2.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

This figure has two parts labeled a and b. Part a shows rows and rows of trough mirrors. Part b shows how a solar thermal plant works. Heat transfer fluid enters a tank via pipes. The tank contains water which is heated. As the heat is exchanged from the pipes to the water, the water becomes steam. The steam travels to a steam turbine. The steam turbine begins to turn which powers a generator. Exhaust steam exits the steam turbine and enters a cooling tower.

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure **1.2.9**). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a) (b)

Figure **1.2.9**: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

Two pictures are shown and labeled a and b. Picture a shows a thermal plant with three tall metal towers. Picture b is an arial picture of the mirrors used at the plant. They are arranged in rows.

Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

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

Glossary

calorie (cal)

unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process

chemical reaction or physical change that absorbs heat

energy

capacity to supply heat or do work

exothermic process

chemical reaction or physical change that releases heat

heat (q)

transfer of thermal energy between two bodies

heat capacity (C)

extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)

SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

kinetic energy

energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where m = mass and v = velocity)

potential energy

energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (*c*)

intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature

intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy

kinetic energy associated with the random motion of atoms and molecules

thermochemistry

study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (*w*)

energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

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1.3: Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure **1.3.1**). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

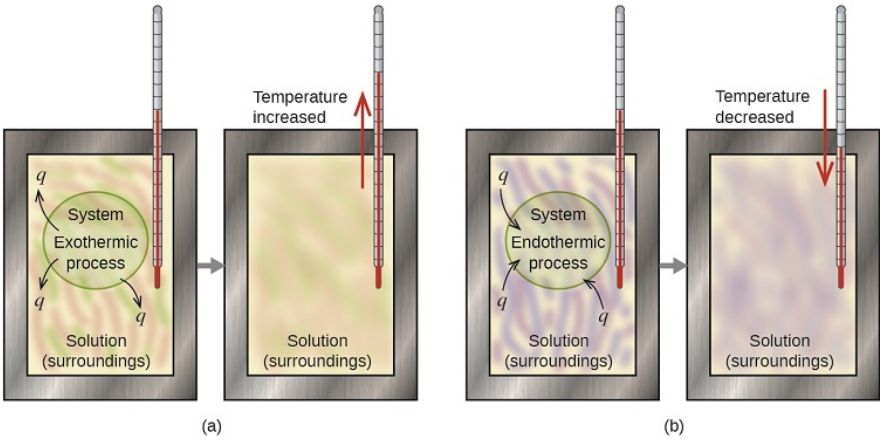


Figure **1.3.1**: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Two diagrams labeled a and b are shown. Each is made up of two rectangular containers with a thermometer inserted into the top right and extending inside. There is a right facing arrow connecting each box in each diagram. The left container in diagram a depicts a pink and green swirling solution with the terms “Exothermic process” and “System” written in the center with arrows facing away from the terms pointing to “q.” The labels “Solution” and “Surroundings” are written at the bottom of the container. The right container in diagram a has the term “Solution” written at the bottom of the container and a red arrow facing up near the thermometer with the phrase “Temperature increased” next to it. The pink and green swirls are more blended in this container. The left container in diagram b depicts a purple and blue swirling solution with the terms “Endothermic process” and “System” written in the center with arrows facing away from the terms and “Solution” and “Surroundings” written at the bottom. The arrows point away from the letter “q.” The right container in diagram b has the term “Solution” written at the bottom and a red arrow facing down near the thermometer with the phrase “Temperature decreased” next to it. The blue and purple swirls are more blended in this container.

By convention, q is given a negative (-) sign when the system releases heat to the surroundings (exothermic); q is given a positive (+) sign when the system absorbs heat from the surroundings (endothermic).

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure **1.3.2**). These easy-to-use “coffee cup” calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

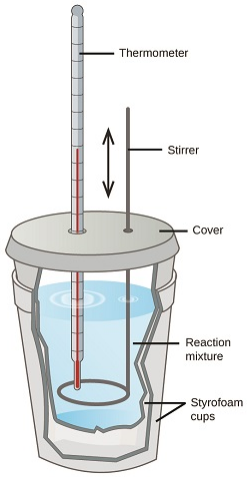


Figure 1.3.2: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Two Styrofoam cups are shown nested in one another with a cover over the top. A thermometer and stirring rod are inserted through the cover and into the solution inside the cup, which is shown as a cut-away. The stirring rod has a double headed arrow next to it facing up and down. The liquid mixture inside the cup is labeled “Reaction mixture.”

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 1.3.3).

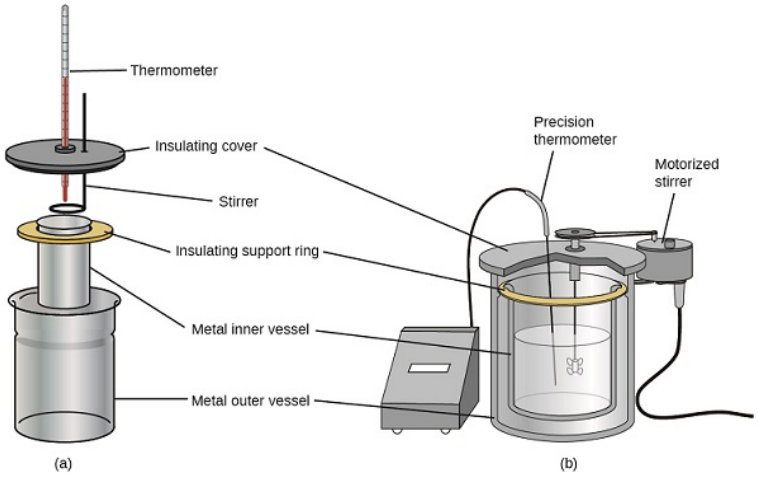


Figure 1.3.3: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Two diagrams are shown and labeled a and b. Diagram a depicts a thermometer which passes through a disk-like insulating cover and into a metal cylinder which is labeled “metal inner vessel,” which is in turn nested in a metal cylinder labeled “metal outer vessel.” The inner cylinder rests on an insulating support ring. A stirrer passes through the insulating cover and into the inner cylinder as well. Diagram b shows an inner metal vessel half full of liquid resting on an insulating support ring and nested in a metal outer vessel. A precision temperature probe and motorized stirring rod are placed into the solution in the inner vessel and connected by wires to equipment exterior to the set-up.

Before we practice calorimetry problems involving chemical reactions, consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 1.3.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter’s surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{1.3.1}$$

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

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{1.3.2}$$

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

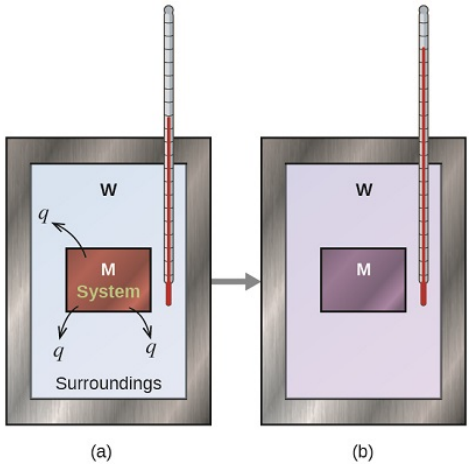


Figure **1.3.4**: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Two diagrams are shown and labeled a and b. Each diagram is composed of a rectangular container with a thermometer inserted inside from the top right corner. Both containers are connected by a right-facing arrow. Both containers are full of water, which is depicted by the letter "W," and each container has a square in the middle which represents a metal which is labeled with a letter "M." In diagram a, the metal is drawn in brown and has three arrows facing away from it. Each arrow has the letter "q" at its end. The metal is labeled "system" and the water is labeled "surroundings." The thermometer in this diagram has a relatively low reading. In diagram b, the metal is depicted in purple and the thermometer has a relatively high reading.

✔ Example 1.3.1: Heat Transfer between Substances at Different Temperatures

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

Solution

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

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

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

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

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

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

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

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

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

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

? Exercise 1.3.1A

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

Answer

The initial temperature of the copper was 335.6 °C.

? Exercise 1.3.1B

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

Answer

The final temperature (reached by both copper and water) is 38.7 °C.

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

✓ Example 1.3.2: Identifying a Metal by Measuring Specific Heat

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

Solution

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

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

In expanded form, this is:

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

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

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

Solving this:

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

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

? Exercise 1.3.2

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

Answer

$c_{metal} = 0.13\ J/g\ °C$

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

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

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{1.3.3}$$

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

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{1.3.4}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example 1.3.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184\ \text{J/g °C})(1.0 \times 10^2\ \text{g})(28.9°\text{C} - 22.0°\text{C}) = 2.89 \times 10^3\ \text{J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.89 \times 10^3\ J$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

Exercise 1.3.3

When 100 mL of 0.200 M NaCl(*aq*) and 100 mL of 0.200 M $AgNO_3$(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer

$1.34 \times 10^3\ J$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 1.3.5). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around

which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\mathbf{NaC_2H_3O_2(\mathit{aq}) \longrightarrow NaC_2H_3O_2(\mathit{s})}$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.



Figure **1.3.5**: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

A series of three photos is shown. There are two right-facing arrows connecting one photo to the next. The first photo shows a chemical hand warmer. It is a bag that contains a clear, colorless liquid. There is a white disk located to the right inside the bag. The second photo shows the same thing, except the white disc has become a white, cloudy substance. The third photo shows the entire bag filled with this white substance.

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$\mathbf{2\,Fe\,(s) + \tfrac{3}{2}\,O_2\,(g) \longrightarrow Fe_2O_3\,(s).}\ \ n$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

✔ Example **1.3.4**: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an "instant ice pack" (Figure **1.3.5**). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.



Figure **1.3.5**: An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{rxn} = -q_{soln}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

https://chem.libretexts.org/@go/page/440671

$$\begin{aligned} q_{rxn} &= -q_{soln} = -(c \times m \times \Delta T)_{soln} \\ &= -[(4.184 J/g\,°C) \times (53.2\,g) \times (20.3°C - 24.9°C)] \\ &= -[(4.184 J/g\,°C) \times (53.2\,g) \times (-4.6°C)] \\ &+ 1.0 \times 10^3\,J = +1.0\,kJ \end{aligned}$$

The positive sign for q indicates that the dissolution is an endothermic process.

? Exercise 1.3.4

When a 3.00-g sample of KCl was added to 3.00 × 10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

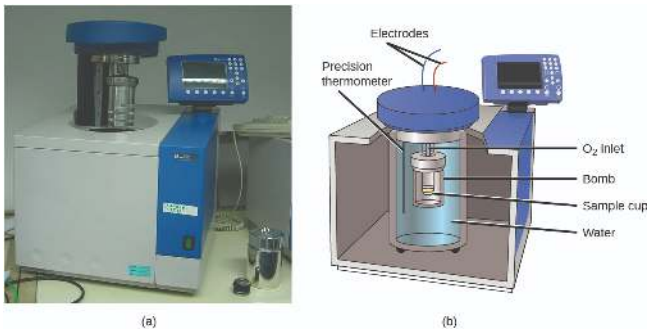
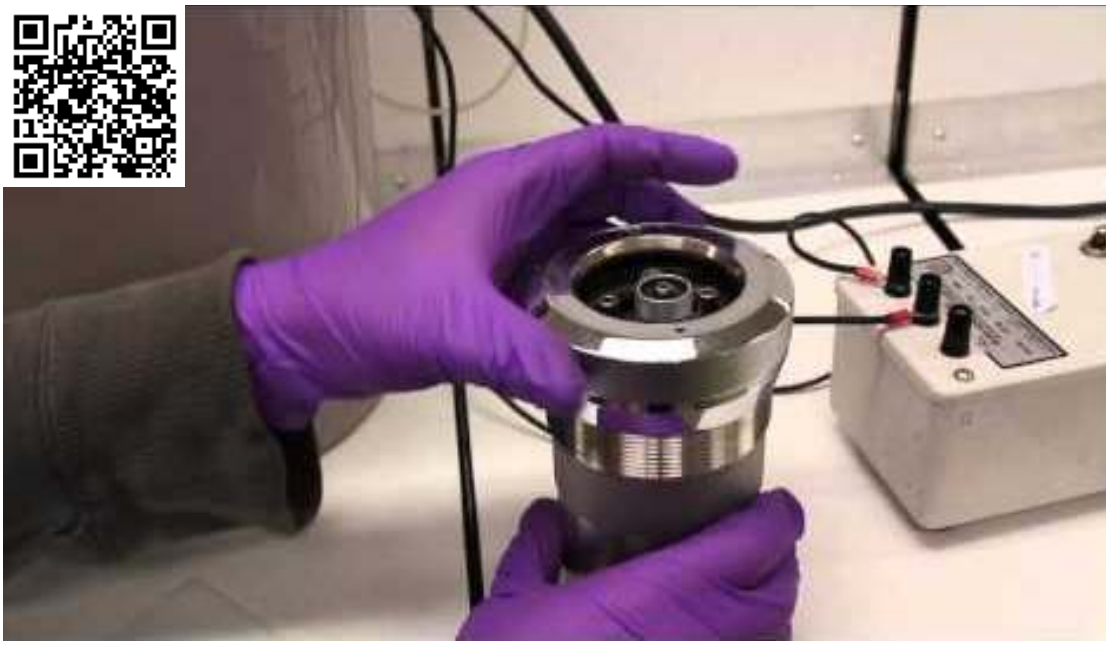


Figure **1.3.6**: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

A picture and a diagram are shown, labeled a and b, respectively. Picture a depicts a bomb calorimeter. It is a cube-shaped machine with a cavity in the top, a metal cylinder that is above the cavity, and a read-out panel attached to the top-right side. Diagram b depicts a cut away figure of a cube with a cylindrical container full of water in the middle of it. Another container, labeled "bomb," sits inside of a smaller cylinder which holds a sample cup and is nested in the cylindrical container surrounded by the water. A black line extends into the water and is labeled "Precision thermometer." Two wires labeled "Electrodes" extend away from a cover that sits on top of the interior container. A read-out panel is located at the top right of the cube.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure **1.3.6**). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.



Video 1.3.1: Video of view how a bomb calorimeter is prepared for action.

Example 1.3.5: Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ &= -[(4.184\ \text{J/g °C}) \times (775\ \text{g}) \times (35.6\text{°C} - 23.8\text{°C}) + 893\ \text{J/°C} \times (35.6\text{°C} - 23.8\text{°C})] \\ &= -(38,300\ \text{J} + 10,500\ \text{J}) \\ &= -48,800\ \text{J} = -48.8\ \text{kJ} \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

Exercise 1.3.5

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Answer

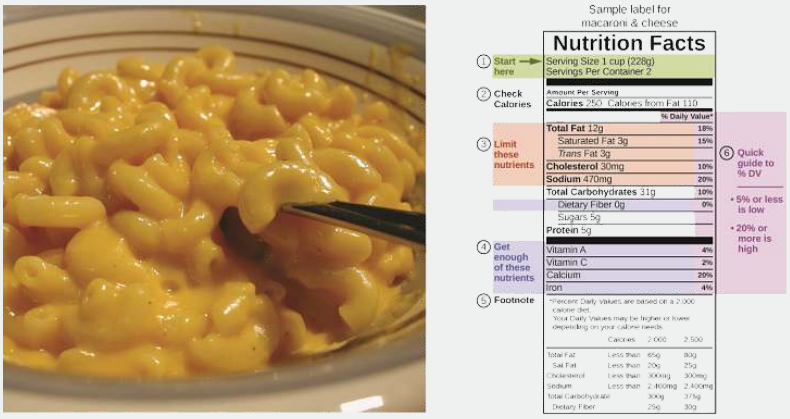
39.0 kJ

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[1] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure **1.3.7**).



(a) (b)

Figure **1.3.7**: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5\text{ g protein} \times 4\text{ Calories/g}) + (31\text{ g carb} \times 4\text{ Calories/g}) + (12\text{ g fat} \times 9\text{ Calories/g}) = 252\text{ Calories} \quad (1.3.5)$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations. Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Footnotes

1. 1 Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, The Snellen human calorimeter revisited, re-engineered and upgraded: design and performance characteristics [link.springer.com].

Glossary

bomb calorimeter

device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter
device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry
process of measuring the amount of heat involved in a chemical or physical process

nutritional calorie (Calorie)
unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings
all matter other than the system being studied

system
portion of matter undergoing a chemical or physical change being studied

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1.4: Enthalpy

Learning Objectives

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

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

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

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

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

$$\Delta U = q + w \tag{1.4.1}$$

as shown in Figure **1.4.1**. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive q is heat flow in; negative q is heat flow out) or work done on or by the system. The work, w, is positive if it is done on the system and negative if it is done by the system.

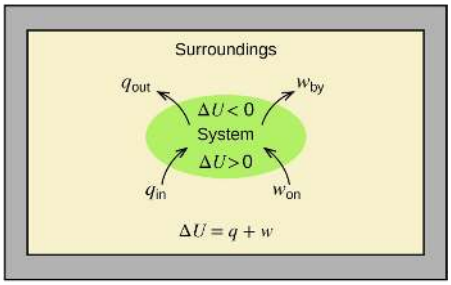


Figure **1.4.1**: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

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

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is a type of quantity known as a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure **1.4.2**). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).



Figure **1.4.2**: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

An aerial photo depicts a view of Mount Kilimanjaro. A straight, green arrow labeled X is drawn from the term "base," written at the bottom of the mountain, to the term "Summit," written at the top of the mountain. Another arrow labeled Y is draw from the base to the summit alongside the green arrow, but this arrow is pink and has three large S-shaped curves along its length.

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

$$H = U + PV \tag{1.4.2}$$

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

$$\Delta H = \Delta U + P\Delta V \tag{1.4.3}$$

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

$$P\Delta V = -w \tag{1.4.4}$$

Substituting Equation 1.4.4 and the definition of internal energy (Equation 1.4.1) into Equation 1.4.3 yields:

$$\Delta H = \Delta U + P\Delta V \tag{1.4.5}$$
$$= q_p + \cancel{w} - \cancel{w} \tag{1.4.6}$$
$$= q_p \tag{1.4.7}$$

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

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

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents expansion work from occurring. Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat.

The following conventions apply when we use ΔH:

1. Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products as shown in the chemical equation. For example, consider this equation:

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)} \quad \Delta H = -286\ \mathrm{kJ} \tag{1.4.8}$$

   This equation indicates that when 1 mole of hydrogen gas and 12 mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property).

$$\begin{aligned} &\textrm{(two-fold increase in amounts)} \\ &\ce{2H2(g) + O2(g) -> 2H2O(l)} \quad \Delta H = 2 \times (-286\ \mathrm{kJ}) = -572\ \mathrm{kJ} \\ &\textrm{(two-fold decrease in amounts)} \\ &\tfrac{1}{2}\ce{H2(g) + \tfrac{1}{4}O2(g) -> \tfrac{1}{2}H2O(l)} \quad \Delta H = \tfrac{1}{2}(-286\ \mathrm{kJ}) = -143\ \mathrm{kJ} \end{aligned} \tag{5.4.7}$$

2. The enthalpy change of a reaction depends on the physical state of the reactants and products of the reaction (whether we have gases, liquids, solids, or aqueous solutions), so these must be shown. For example, when 1 mole of hydrogen gas and 12 mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(g)} \quad \Delta H = -242\ \mathrm{kJ} \tag{1.4.9}$$

3. A negative value of an enthalpy change, Δ*H*, indicates an exothermic reaction; a positive value of Δ*H* indicates an endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its Δ*H* is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

Example 1.4.1: Measurement of an Enthalpy Change

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. What is ΔH, the enthalpy change, per mole of acid reacting, for the acid-base reaction run under the conditions described ?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. This ratio

$$\frac{-2.9\ \mathrm{kJ}}{0.0500\ \mathrm{mol\ HCl}}$$

can be used as a conversion factor to find the heat produced when 1 mole of HCl reacts:

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

The enthalpy change when 1 mole of HCl reacts is −58 kJ. Since that is the number of moles in the chemical equation, we write the thermochemical equation as:

$$\mathrm{HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}} \quad \Delta H = -58\ \mathrm{kJ}$$

Exercise 1.4.1

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

$$\mathrm{Zn_{(s)} + 2\,HCl_{(aq)} \longrightarrow ZnCl_{(aq)} + H_{2(g)}}$$

Answer

ΔH = −153 kJ

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

Example 1.4.2: Another Example of the Measurement of an Enthalpy Change

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Determine the enthalpy change for the reaction

$$\mathrm{C_{12}H_{22}O_{11}(\mathit{aq}) + 8\,KClO_3(\mathit{aq}) \longrightarrow 12\,CO_2(\mathit{g}) + 11\,H_2O(\mathit{l}) + 8\,KCl(\mathit{aq})}$$

Solution

We have $2.67\ \cancel{\mathrm{g}} \times \frac{1\ \mathrm{mol}}{342.3\ \cancel{\mathrm{g}}} = 0.00780\ \mathrm{mol\ C_{12}H_{22}O_{11}}$ available, and

$7.19\ \cancel{\mathrm{g}} \times \frac{1\ \mathrm{mol}}{122.5\ \cancel{\mathrm{g}}} = 0.0587\ \mathrm{mol\ KClO_3}$ available.

Since

$$0.0587\ \mathrm{mol\ KClO_3} \times \frac{1\ \mathrm{mol\ C_{12}H_{22}O_{11}}}{8\ \mathrm{mol\ KClO_3}} = 0.00734\ \mathrm{mol\ C_{12}H_{22}O_{11}}$$

is needed, $C_{12}H_{22}O_{11}$ is the excess reactant and $KClO_3$ is the limiting reactant.

The reaction uses 8 mol $KClO_3$, and the conversion factor is $\frac{-43.7\ \text{kJ}}{0.0587\ \text{mol KClO}_3}$, so we have $\Delta H = 8\ \text{mol} \times \frac{-43.7\ \text{kJ}}{0.0587\ \text{mol KClO}_3} = -5960\ \text{kJ}$. The enthalpy change for this reaction is −5960 kJ, and the thermochemical equation is:

$$C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl \quad \Delta H = -5960\ kJ$$

? Exercise 1.4.2

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_{2(s)}$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2\,(s)$ is produced?

Answer

ΔH = −338 kJ

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and **does not specify a temperature** (it used too). Many thermochemical tables list values with a standard state of 1 atm. Because the Δ*H* of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), Δ*H* values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol (ΔH°_{298}) is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol Δ*H* is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

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

Enthalpy of Combustion

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

$$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2 + 3\,H_2O(l) \quad \Delta H^\circ_{298} = -1366.8\ \text{kJ} \tag{1.4.10}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table **1.4.1**. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table **1.4.1**: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion $\Delta H^\circ_c\left(\frac{\text{kJ}}{\text{mol}}\ \text{at 25°C}\right)$
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	−393.5
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	−285.8
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	−601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	−296.8
carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	−283.0
methane	$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$	−890.8
acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2\,CO_2(g) + H_2O(l)$	−1301.1
ethanol	$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow CO_2(g) + 3\,H_2O(l)$	−1366.8
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$	−726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(l)$	−5461

✓ Example 1.4.3: Using Enthalpy of Combustion

As Figure **1.4.3** suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure **1.4.3**: The combustion of gasoline is very exothermic. (credit: modification of work by "AlexEagle"/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table **1.4.1** gives this value as −5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

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

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

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

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

? Exercise 1.4.3

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

Answer

6.25×10^3 kJ

Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure **1.4.4**). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.



Figure **1.4.4**: (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than $\frac{1}{7}$ of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon. The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure **1.4.5**).



Figure **1.4.5**: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Standard Enthalpy of Formation

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

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

$$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = -393.5\ \text{kJ} \tag{1.4.11}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $\text{NO}_{2(g)}$, ΔH_f° is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\frac{1}{2}\text{N}_2(g) + \text{O}_2(g) \longrightarrow \text{NO}_2(g) \quad \Delta H_f^\circ = \Delta H_{298}^\circ = +33.2\ \text{kJ} \tag{1.4.12}$$

A reaction equation with $\frac{1}{2}$ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $NO_2(g)$.

You will find a table of standard enthalpies of formation of many common substances in Tables T1 and T2. These values indicate that formation reactions range from highly exothermic (such as −2984 kJ/mol for the formation of P_4O_{10}) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, C_2H_2). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

✓ Example 1.4.4: Evaluating an Enthalpy of Formation

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

$$3\,\text{O}_2(g) \longrightarrow 2\,\text{O}_3(g) \quad \Delta H_{298}^\circ = +286\ \text{kJ}$$

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

$$\frac{3}{2}\text{O}_2(g) \longrightarrow \text{O}_3(g)$$

For the formation of 2 mol of $O_3(g)$, $\Delta H^\circ_{298} = +286\ kJ$. This ratio, $\left(\frac{286\ kJ}{2\ mol\ O_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $O_3(g)$:

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

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

? Exercise 1.4.4

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

Answer

For the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H^\circ_{298} = -184.6\ kJ$$

✓ Example 1.4.5: Writing Reaction Equations for ΔH_f°

Write the heat of formation reaction equations for:

a. $C_2H_5OH_{(l)}$
b. $Ca_3(PO_4)_{2(s)}$

Solution

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

a. $2\,C(s,\ graphite) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$
b. $3\,Ca(s) + \frac{1}{2}P_4(s) + 4\,O_2(g) \longrightarrow Ca_3(PO_4)_2(s)$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

? Exercise 1.4.5

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_{5(l)}$
b. $Na_2CO_{3(s)}$

Answer a

$4\,C(s,\ graphite) + 5\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OC_2H_5(l)$;

Answer b

$2\,Na(s) + C(s,\ graphite) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$

Hess's Law

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

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

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H^\circ_{298} = -394\ kJ \tag{1.4.13}$$

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

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \quad \Delta H^\circ_{298} = -111\ kJ \tag{1.4.14}$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H^\circ_{298} = -283\ kJ \tag{1.4.15}$$

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

$$\begin{aligned}
&\text{Step 1: } C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g)\\
&\text{Step 2: } CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g)\\
&\text{Sum: } C(s) + \tfrac{1}{2}O_2(g) + CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) + CO_2(g)
\end{aligned}$$

Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \tag{1.4.16}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps. We can apply the data from the experimental enthalpies of combustion in Table **1.4.1** to find the enthalpy change of the entire reaction from its two steps:

$$\begin{aligned}
&C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) && \Delta H^\circ_{298} = -111\ kJ\\
&CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) && \Delta H^\circ_{298} = -283\ kJ\\
&\overline{C(s) + O_2(g) \longrightarrow CO_2(g)} && \overline{\Delta H^\circ_{298} = -394\ kJ}
\end{aligned}$$

The result is shown in Figure **1.4.6**. We see that ΔH of the overall reaction is the same whether it occurs in one step or two. This finding (overall ΔH for the reaction = sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

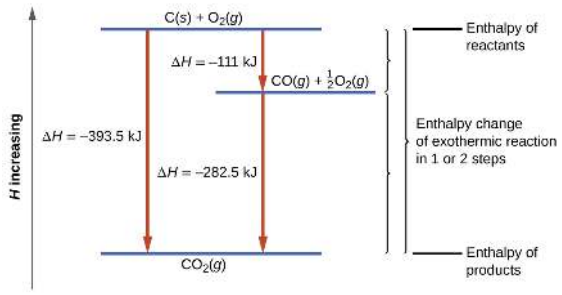


Figure **1.4.6**: The formation of CO_2(g) from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

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

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

$$\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H = +33.2\ \text{kJ} \tag{1.4.17}$$

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

$$N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g) \quad \Delta H = +66.4\ \text{kJ} \tag{1.4.18}$$

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

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

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H = -184.6\ \text{kJ} \tag{1.4.19}$$

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

$$2\,HCl(g) \longrightarrow H_2(g) + Cl_2(g) \quad \Delta H = +184.6\ \text{kJ} \tag{1.4.20}$$

Example 1.4.6: Stepwise Calculation of ΔH_f°

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

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

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

Solution

We are trying to find the standard enthalpy of formation of FeCl3(s), which is equal to ΔH° for the reaction:

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

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

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

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

Exercise 1.4.6

Calculate ΔH for the process:

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

from the following information:

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

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

Answer

66.4 kJ

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

Example 1.4.7: A More Challenging Problem

Using Hess's Law Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

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

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

$$\text{(ii)}\ 2\,OF_2(g) \longrightarrow O_2(g) + 2\,F_2(g) \quad \Delta H_{(ii)}^\circ = -49.4\ \text{kJ}$$

$$\text{(iii)}\ 2\,ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g) \quad \Delta H_{(iii)}^\circ = +205.6\ \text{kJ}$$

$$\text{(iv) } \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \longrightarrow \tfrac{1}{2}\mathrm{Cl_2O}(g) + \tfrac{3}{2}\mathrm{OF_2}(g) \quad \Delta H^\circ_{\text{(iv)}} = +266.7\ \mathrm{kJ}$$

Solution

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

$$\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) \quad \Delta H^\circ = \frac{1}{2}(205.6) = +102.8\ k\mathrm{J}$$

Next, we see that $\mathrm{F_2}$ is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH° changes sign and is halved:

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

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

$$\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) \quad \Delta H^\circ = -266.7\ \mathrm{kJ}$$

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

$$\begin{array}{ll}
\mathrm{ClF}(g) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \frac{1}{2}\mathrm{Cl_2O}(g) + \frac{1}{2}\mathrm{OF_2}(g) & \Delta H^\circ = +102.8\ \mathrm{kJ} \\
\frac{1}{2}\mathrm{O_2}(g) + \mathrm{F_2}(g) \longrightarrow \mathrm{OF_2}(g) & \Delta H^\circ = +24.7\ \mathrm{kJ} \\
\frac{1}{2}\mathrm{Cl_2O}(g) + \frac{3}{2}\mathrm{OF_2}(g) \longrightarrow \mathrm{ClF_3}(g) + \mathrm{O_2}(g) & \Delta H^\circ = -266.7\ \mathrm{kJ} \\
\hline
\mathrm{ClF}(g) + \mathrm{F_2} \longrightarrow \mathrm{ClF_3}(g) & \Delta H^\circ = -139.2\ \mathrm{kJ}
\end{array}$$

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

$$\Delta H^\circ = (+102.8\ \mathrm{kJ}) + (24.7\ \mathrm{kJ}) + (-266.7\ \mathrm{kJ}) = -139.2\ \mathrm{kJ}$$

? Exercise 1.4.7

Aluminum chloride can be formed from its elements:

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

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

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

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

$$\text{(iv) } \mathrm{AlCl_3}(aq) \longrightarrow \mathrm{AlCl_3}(s) \quad \Delta H^\circ_{\text{(iv)}} = +323\ \mathrm{kJ/mol}$$

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

Answer

−1407 kJ

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are: (i) decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by (ii) re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products). The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with $\sum$ representing "the sum of" and n standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{products}) - \sum n \times \Delta H^\circ_f(\text{reactants}) \tag{1.4.21}$$

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

✓ Example 1.4.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

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

Solution 1: Using the Equation

Alternatively, we could use the special form of Hess's law given previously:

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

$$= \left[2\ \cancel{\text{mol HNO}_3} \times \frac{-207.4\ \text{kJ}}{\cancel{\text{mol HNO}_3\ (aq)}} + 1\ \cancel{\text{mol NO}\ (g)} \times \frac{+90.2\ \text{kJ}}{\cancel{\text{mol NO}\ (g)}}\right]$$

$$- \left[3\ \cancel{\text{mol NO}_2(g)} \times \frac{+33.2\ \text{kJ}}{\cancel{\text{mol NO}_2\ (g)}} + 1\ \cancel{\text{mol H}_2\text{O}\ (l)} \times \frac{-285.8\ \text{kJ}}{\cancel{\text{mol H}_2\text{O}\ (l)}}\right]$$

$$= 2(-207.4\ \text{kJ}) + 1(+90.2\ \text{kJ}) - 3(+33.2\ \text{kJ}) - 1(-285.8\ \text{kJ})$$

$$= -138.4\ \text{kJ}$$

Solution 2: Supporting Why the General Equation Is Valid

We can write this reaction as the sum of the decompositions of $3NO_2(g)$ and $1H_2O(l)$ into their constituent elements, and the formation of 2 $HNO_3(aq)$ and 1 NO(g) from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH°_f values for these compounds (from Tables T1 and T2), we have:

$$3\,\mathrm{NO_2}(g) \longrightarrow \frac{3}{2}\mathrm{N_2}(g) + 3\mathrm{O_2}(g) \quad \Delta H^\circ_1 = -99.6\ \mathrm{kJ}$$

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2}(g) + \frac{1}{2}\mathrm{O_2}(g) \quad \Delta H^\circ_2 = +285.8\ k\mathrm{J}\ [-1 \times \Delta H^\circ_f(\mathrm{H_2O})]$$

$$\mathrm{H_2}(g) + \mathrm{N_2}(g) + 3\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{HNO_3}(aq) \quad \Delta H^\circ_3 = -414.8\ k\mathrm{J}\ [2 \times \Delta H^\circ_f(\mathrm{HNO_3})]$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \quad \Delta H_4^\circ = +90.2\ kJ\ [1 \times (NO)]$$

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

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

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

$$\begin{aligned}\Delta H_{rxn}^\circ &= \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ \\ &= (-99.6\ kJ) + (+285.8\ kJ) + (-414.8\ kJ) + (+90.2\ kJ) \\ &= -138.4\ kJ\end{aligned}$$

So the standard enthalpy change for this reaction is $\Delta H^\circ = -138.4$ kJ.

Note that this result was obtained by:

1. multiplying the ΔH_f° of each product by its stoichiometric coefficient and summing those values,
2. multiplying the ΔH_f° of each reactant by its stoichiometric coefficient and summing those values, and then
3. subtracting the result found in step 2 from the result found in step 1.

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

? Exercise 1.4.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH(l)$, when $H_2O(l)$ and $CO_2(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH(l)$, −278 kJ/mol; $H_2O(l)$, −286 kJ/mol; and $CO_2(g)$, −394 kJ/mol.

Answer

−1368 kJ/mol

Summary

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH_{298}° for reactions occurring under standard state conditions. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. Examples of enthalpy changes include enthalpy of combustion, enthalpy of fusion, enthalpy of vaporization, and standard enthalpy of formation. The standard enthalpy of formation, ΔH_f°, is the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar (standard state). Many of the processes are carried out at 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

Key Equations

- $\Delta U = q + w$
- $\Delta H_{reaction}^\circ = \sum n \times \Delta H_f^\circ(\text{products}) - \sum n \times \Delta H_f^\circ(\text{reactants})$

Footnotes

1. 1 For more on algal fuel, see www.theguardian.com/environme...n-fuel-problem.

Glossary

chemical thermodynamics
area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

enthalpy (H)
sum of a system's internal energy and the mathematical product of its pressure and volume

enthalpy change (ΔH)
heat released or absorbed by a system under constant pressure during a chemical or physical process

expansion work (pressure-volume work)
work done as a system expands or contracts against external pressure

first law of thermodynamics
internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

Hess's law
if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (U)
total of all possible kinds of energy present in a substance or substances

standard enthalpy of combustion (ΔH_c°)
heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation (ΔH_f°)
enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

standard state
set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

state function
property depending only on the state of a system, and not the path taken to reach that state

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1.5: Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol⁻)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
aluminum			
Al(s)	0	0	28.3
Al(g)	324.4	285.7	164.54
$Al^{3+}(aq)$	-531	-485	-321.7
$Al_2O_3(s)$	–1676	–1582	50.92
$AlF_3(s)$	–1510.4	–1425	66.5
$AlCl_3(s)$	–704.2	–628.8	110.67
$AlCl_3{\cdot}6H_2O(s)$	–2691.57	–2269.40	376.56
$Al_2S_3(s)$	–724.0	–492.4	116.9
$Al_2(SO_4)_3(s)$	–3445.06	–3506.61	239.32
antimony			
Sb(s)	0	0	45.69
Sb(g)	262.34	222.17	180.16
$Sb_4O_6(s)$	–1440.55	–1268.17	220.92
$SbCl_3(g)$	–313.8	–301.2	337.80
$SbCl_5(g)$	–394.34	–334.29	401.94
$Sb_2S_3(s)$	–174.89	–173.64	182.00
$SbCl_3(s)$	–382.17	–323.72	184.10
SbOCl(s)	–374.0	—	—
arsenic			
As(s)	0	0	35.1
As(g)	302.5	261.0	174.21
$As_4(g)$	143.9	92.4	314
$As_4O_6(s)$	–1313.94	–1152.52	214.22
$As_2O_5(s)$	–924.87	–782.41	105.44
$AsCl_3(g)$	–261.50	–248.95	327.06
$As_2S_3(s)$	–169.03	–168.62	163.59
$AsH_3(g)$	66.44	68.93	222.78
$H_3AsO_4(s)$	–906.3	—	—
barium			
Ba(s)	0	0	62.5
Ba(g)	180	146	170.24

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Ba^{2+}(aq)$	-537.6	-560.8	9.6
BaO(*s*)	–548.0	–520.3	72.1
$BaCl_2(s)$	–855.0	–806.7	123.7
$BaSO_4(s)$	–1473.2	–1362.3	132.2
beryllium			
Be(*s*)	0	0	9.50
Be(*g*)	324.3	286.6	136.27
BeO(*s*)	–609.4	–580.1	13.8
bismuth			
Bi(*s*)	0	0	56.74
Bi(*g*)	207.1	168.2	187.00
$Bi_2O_3(s)$	–573.88	–493.7	151.5
$BiCl_3(s)$	–379.07	–315.06	176.98
$Bi_2S_3(s)$	–143.1	–140.6	200.4
boron			
B(*s*)	0	0	5.86
B(*g*)	565.0	521.0	153.4
$B_2O_3(s)$	–1273.5	–1194.3	53.97
$B_2H_6(g)$	36.4	87.6	232.1
$H_3BO_3(s)$	–1094.33	–968.92	88.83
$BF_3(g)$	–1136.0	–1119.4	254.4
$BCl_3(g)$	–403.8	–388.7	290.1
$B_3N_3H_6(l)$	–540.99	–392.79	199.58
$HBO_2(s)$	–794.25	–723.41	37.66
bromine			
$Br_2(l)$	0	0	152.23
$Br_2(g)$	30.91	3.142	245.5
Br(*g*)	111.88	82.429	175.0
$Br^-(aq)$	-120.9	-102.82	80.71
$BrF_3(g)$	–255.60	–229.45	292.42
HBr(*g*)	–36.3	–53.43	198.7
cadmium			
Cd(*s*)	0	0	51.76
Cd(*g*)	112.01	77.41	167.75

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Cd^{2+}(aq)$	-75.90	-77.61	-73.2
CdO(*s*)	–258.2	–228.4	54.8
$CdCl_2(s)$	–391.5	–343.9	115.3
$CdSO_4(s)$	–933.3	–822.7	123.0
CdS(*s*)	–161.9	–156.5	64.9
calcium			
Ca(*s*)	0	0	41.6
Ca(*g*)	178.2	144.3	154.88
$Ca^{2+}(aq)$	-542.96	-553.04	-55.2
CaO(*s*)	–634.9	–603.3	38.1
$Ca(OH)_2(s)$	–985.2	–897.5	83.4
$CaSO_4$(s)	–1434.5	–1322.0	106.5
$CaSO_4 \cdot 2H_2O(s)$	–2022.63	–1797.45	194.14
$CaCO_3$(s) (calcite)	–1220.0	–1081.4	110.0
$CaSO_3 \cdot H_2O(s)$	–1752.68	–1555.19	184.10
carbon			
C(*s*) (graphite)	0	0	5.740
C(*s*) (diamond)	1.89	2.90	2.38
C(*g*)	716.681	671.2	158.1
CO(*g*)	–110.52	–137.15	197.7
$CO_2(g)$	–393.51	–394.36	213.8
$CO_3^{2-}(aq)$	-677.1	-527.8	-56.9
$CH_4(g)$	–74.6	–50.5	186.3
$CH_3OH(l)$	–239.2	–166.6	126.8
$CH_3OH(g)$	–201.0	–162.3	239.9
$CCl_4(l)$	–128.2	–62.5	214.4
$CCl_4(g)$	–95.7	–58.2	309.7
$CHCl_3(l)$	–134.1	–73.7	201.7
$CHCl_3(g)$	–103.14	–70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3^-\,(aq)$	-691.11	-587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+\,(aq)$	-248	-282.0	133
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-\,(aq)$	-167.2	-131.2	56.5
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$CrO_4^{2-}\,(aq)$	-881.2	-727.8	50.21
$Cr_2O_7^{2-}\,(aq)$	-1490.3	-1301.1	261.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$Co^{2+}(aq)$	-67.4	-51.5	-155
$Co^{3+}(aq)$	92	134	-305.0
$CoO(s)$	–237.9	–214.2	52.97
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
$Cu^{+}(aq)$	51.9	50.2	-26
$Cu^{2+}(aq)$	64.77	65.49	-99.6
$CuO(s)$	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
$CuS(s)$	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
$F(g)$	79.4	62.3	158.8
$F^{-}(aq)$	-332.6	-278.8	-13.8
$F_2O(g)$	24.7	41.9	247.43
$HF(g)$	–273.3	–275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
$H(g)$	217.97	203.26	114.7
$H^{+}(aq)$	0	0	0
$OH^{-}(aq)$	-230.0	-157.2	-10.75
$H_3O^{+}(aq)$	-285.8		69.91
$H_2O(l)$	–285.83	–237.1	70.0

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_2O(g)$	–241.82	–228.59	188.8
$H_2O_2(l)$	–187.78	–120.35	109.6
$H_2O_2(g)$	–136.3	–105.6	232.7
$HF(g)$	–273.3	–275.4	173.8
$HCl(g)$	–92.307	–95.299	186.9
$HBr(g)$	–36.3	–53.43	198.7
$HI(g)$	26.48	1.70	206.59
$H_2S(g)$	–20.6	–33.4	205.8
$H_2Se(g)$	29.7	15.9	219.0
iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.3	260.7
$I(g)$	106.84	70.2	180.8
$I^-(aq)$	-55.19	-51.57	11.13
$IF(g)$	95.65	–118.49	236.06
$ICl(g)$	17.78	–5.44	247.44
$IBr(g)$	40.84	3.72	258.66
$IF_7(g)$	–943.91	–818.39	346.44
$HI(g)$	26.48	1.70	206.59
iron			
$Fe(s)$	0	0	27.3
$Fe(g)$	416.3	370.7	180.5
$Fe^{2+}(aq)$	-89.1	-78.90	-137.7
$Fe^{3+}(aq)$	-48.5	-4.7	-315.9
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(CO)_5(l)$	–774.04	–705.42	338.07
$Fe(CO)_5(g)$	–733.87	–697.26	445.18
$FeCl_2(s)$	–341.79	–302.30	117.95
$FeCl_3(s)$	–399.49	–334.00	142.3
$FeO(s)$	–272.0	–255.2	60.75
$Fe(OH)_2(s)$	–569.0	–486.5	88.
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
$FeS(s)$	–100.0	–100.4	60.29

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$Fe_3C(s)$	25.10	20.08	104.60
lead			
$Pb(s)$	0	0	64.81
$Pb(g)$	195.2	162.	175.4
$Pb^{2+}(aq)$	-1.7	-24.43	10.5
PbO(s) (yellow)	–217.32	–187.89	68.70
PbO(s) (red)	–218.99	–188.93	66.5
$Pb(OH)_2(s)$	–515.9	—	—
$PbS(s)$	–100.4	–98.7	91.2
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
$Li(s)$	0	0	29.1
$Li(g)$	159.3	126.6	138.8
$Li^+(aq)$	-278.5	-293.3	13.4
$LiH(s)$	–90.5	–68.3	20.0
$Li(OH)(s)$	–487.5	–441.5	42.8
$LiF(s)$	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
magnesium			
$Mg^{2+}(aq)$	-466.9	-454.8	-138.1
manganese			
$Mn(s)$	0	0	32.0
$Mn(g)$	280.7	238.5	173.7
$Mn^{2+}(aq)$	-220.8	-228.1	-73.6
$MnO(s)$	–385.2	–362.9	59.71
$MnO_2(s)$	–520.03	–465.1	53.05
$Mn_2O_3(s)$	–958.97	–881.15	110.46
$Mn_3O_4(s)$	–1378.83	–1283.23	155.64
$MnO_4^-(aq)$	-541.4	-447.2	191.2
$MnO_4^{2-}(aq)$	-653.0	-500.7	59
mercury			
$Hg(l)$	0	0	75.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Hg(g)	61.4	31.8	175.0
$Hg^{2+}(aq)$		164.8	
$Hg_2^{2+}(aq)$	172.4	153.9	84.5
HgO(s) (red)	–90.83	–58.5	70.29
HgO(s) (yellow)	–90.46	–58.43	71.13
$HgCl_2(s)$	–224.3	–178.6	146.0
$Hg_2Cl_2(s)$	–265.4	–210.7	191.6
HgS(s) (red)	–58.16	–50.6	82.4
HgS(s) (black)	–53.56	–47.70	88.28
$HgSO_4(s)$	–707.51	–594.13	0.00
nitrogen			
$N_2(g)$	0	0	191.6
N(g)	472.704	455.5	153.3
NO(g)	90.25	87.6	210.8
$NO_2(g)$	33.2	51.30	240.1
$N_2O(g)$	81.6	103.7	220.0
$N_2O_3(g)$	83.72	139.41	312.17
$NO_3^-(aq)$	-205.0	-108.7	146.4
$N_2O_4(g)$	11.1	99.8	304.4
$N_2O_5(g)$	11.3	115.1	355.7
$NH_3(g)$	–45.9	–16.5	192.8
$NH_4^+(aq)$	-132.5	-79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
O(g)	249.17	231.7	161.1

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$PO_4^{3-}(aq)$	-1277	-1019	-222
$HPO_3(s)$	–948.5	—	—
$HPO_4^{2-}(aq)$	-1292.1	-1089.3	-33
$H_2PO_4^-(aq)$	-1296.3	-1130.4	90.4
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
$K(s)$	0	0	64.7
$K(g)$	89.0	60.5	160.3
$K^+(aq)$	-252.4	-283.3	102.5
$KF(s)$	–576.27	–537.75	66.57
$KCl(s)$	–436.5	–408.5	82.6
rubidium			
$Rb^+(aq)$	-246	-282.2	124
silicon			
$Si(s)$	0	0	18.8
$Si(g)$	450.0	405.5	168.0
$SiO_2(s)$	–910.7	–856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_2SiO_3(s)$	–1188.67	–1092.44	133.89
$H_4SiO_4(s)$	–1481.14	–1333.02	192.46
$SiF_4(g)$	–1615.0	–1572.8	282.8
$SiCl_4(l)$	–687.0	–619.8	239.7
$SiCl_4(g)$	–662.75	–622.58	330.62
SiC(*s*, *beta cubic*)	–73.22	–70.71	16.61
SiC(*s*, *alpha hexagonal*)	–71.55	–69.04	16.48
silver			
Ag(*s*)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89
$Ag^+(aq)$	105.6	77.11	72.68
$Ag_2O(s)$	–31.05	–11.20	121.3
AgCl(*s*)	–127.0	–109.8	96.3
$Ag_2S(s)$	–32.6	–40.7	144.0
sodium			
Na(*s*)	0	0	51.3
Na(*g*)	107.5	77.0	153.7
$Na^+(aq)$	-240.1	-261.9	59
$Na_2O(s)$	–414.2	–375.5	75.1
NaCl(*s*)	–411.2	–384.1	72.1
strontium			
$Sr^{2+}(aq)$	-545.8	-557.3	-32.6
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
S(*g*)	278.81	238.25	167.82
$S^{2-}(aq)$	41.8	83.7	22
$SO_2(g)$	–296.83	–300.1	248.2
$SO_3(g)$	–395.72	–371.06	256.76
$SO_4^{2-}(aq)$	-909.3	-744.5	20.1
$S_2O_3^{2-}(aq)$	-648.5	-522.5	67
$H_2S(g)$	–20.6	–33.4	205.8
$HS^-(aq)$	-17.7	12.6	61.1
$H_2SO_4(l)$	–813.989	690.00	156.90
$HSO_4^-(aq)$	-885.75	-752.87	126.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5
SnO(s)	–285.8	–256.9	56.5
$SnO_2(s)$	–577.6	–515.8	49.0
$SnCl_4(l)$	–511.3	–440.1	258.6
$SnCl_4(g)$	–471.5	–432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
$TiO_2(s)$	–944.0	–888.8	50.6
$TiCl_4(l)$	–804.2	–737.2	252.4
$TiCl_4(g)$	–763.2	–726.3	353.2
tungsten			
W(s)	0	0	32.6
W(g)	849.4	807.1	174.0
$WO_3(s)$	–842.9	–764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(g)	130.73	95.14	160.98
$Zn^{2+}(aq)$	-153.9	-147.1	-112.1
ZnO(s)	–350.5	–320.5	43.7
$ZnCl_2(s)$	–415.1	–369.43	111.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$ZnS(s)$	–206.0	–201.3	57.7
$ZnSO_4(s)$	–982.8	–871.5	110.5
$ZnCO_3(s)$	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

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1.6: Bond Energies

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.*

When a chemical reaction occurs, molecular bonds are broken and other bonds are formed to make different molecules. For example, the bonds of two water molecules are broken to form hydrogen and oxygen.

$$2\,H_2O \rightarrow 2\,H_2 + O_2$$

Energy is always required to break a bond, which is known as bond energy. While the concept may seem simple, bond energy serves a very important purpose in describing the structure and characteristics of a molecule. It can be used to determine which Lewis Dot Structure is most suitable when there are multiple Lewis Dot Structures.

> *Energy is always required to break a bond. Energy is released when a bond is made.*

Bond enthalpy, also known as bond energy, represents the average energy required to break one mole of a specific type of bond in the gaseous state, while enthalpy is a measure of the total heat content of a system, and bond breaking is always endothermic (requires energy), and bond formation is exothermic (releases energy). Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. We can calculate a more general bond energy by finding the average of the bond energies of a specific bond in different molecules to get the average bond energy.

Table 1: Average Bond Energies (kJ/mol)

Single Bonds						Multiple Bonds	
H—H	432	**N—H**	391	**I—I**	149	**C = C**	614
H—F	565	**N—N**	160	**I—Cl**	208	**C ≡ C**	839
H—Cl	427	**N—F**	272	**I—Br**	175	**O = O**	495
H—Br	363	**N—Cl**	200			**C = O***	745
H—I	295	**N—Br**	243	**S—H**	347	**C ≡ O**	1072
		N—O	201	**S—F**	327	**N = O**	607
C—H	413	**O—H**	467	**S—Cl**	253	**N = N**	418
C—C	347	**O—O**	146	**S—Br**	218	**N ≡ N**	941
C—N	305	**O—F**	190	**S—S**	266	**C ≡ N**	891
C—O	358	**O—Cl**	203			**C = N**	615
C—F	485	**O—I**	234	**Si—Si**	340		
C—Cl	339			**Si—H**	393		
C—Br	276	**F—F**	154	**Si—C**	360		
C—I	240	**F—Cl**	253	**Si—O**	452		
C—S	259	**F—Br**	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C == O(CO_2) = 799

When a bond is strong, there is a higher bond energy because it takes more energy to break a strong bond. This correlates with bond order and bond length. When the Bond order is higher, bond length is shorter, and the shorter the bond length means a greater the Bond Energy because of increased electric attraction. In general, **the shorter the bond length, the greater the bond energy.**

The average bond energies in Table T3 are the averages of bond dissociation energies. For example the average bond energy of O-H in H_2O is 464 kJ/mol. This is due to the fact that the H-OH bond requires 498.7 kJ/mol to dissociate, while the O-H bond needs 428 kJ/mol.

$$\frac{498.7\ kJ/mol + 428\ kJ/mol}{2} = 464\ kJ/mol \tag{1.6.1}$$

When more bond energies of the bond in different molecules that are taken into consideration, the average will be more accurate. However,

- Average bonds values are not as accurate as a molecule specific bond-dissociation energies.
- Double bonds are higher energy bonds in comparison to a single bond (but not necessarily 2-fold higher).
- Triple bonds are even higher energy bonds than double and single bonds (but not necessarily 3-fold higher).

Bond Breakage and Formation

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*.

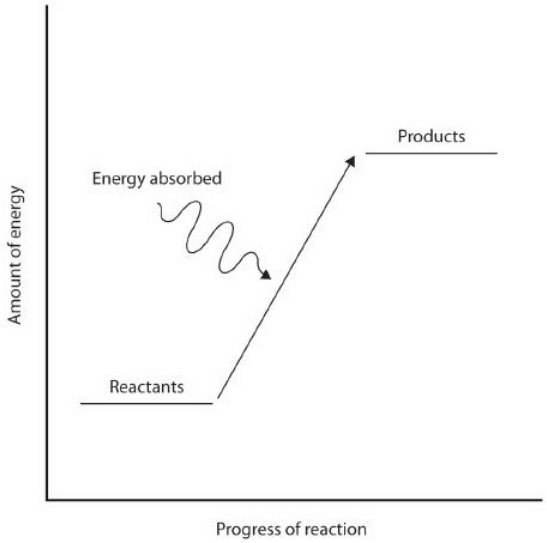


Figure 1: (**left**) Exothermic Reactions. For an exothermic chemical reaction, energy is given off as reactants are converted to products. **(right)** Endothermic Reactions. For an endothermic chemical reaction, energy is absorbed as reactants are converted to products.

In some reactions, the energy of the products is lower than the energy of the reactants. Thus, in the course of the reaction, the substances lose energy to the surrounding environment. Such reactions are exothermic and can be represented by an *energy-level diagram* in Figure 1 (left). In most cases, the energy is given off as heat (although a few reactions give off energy as light). In chemical reactions where the products have a higher energy than the reactants, the reactants must absorb energy from their environment to react. These reactions are endothermic and can be represented by an energy-level diagrams like Figure 1 (right).

Technically 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.

Exothermic and endothermic reactions can be thought of as having energy as either a "product" of the reaction or a "reactant." Exothermic reactions releases energy, so energy is a product. Endothermic reactions require energy, so energy is a reactant.

Example 1.6.1: Exothermic vs. Endothermic

Is each chemical reaction exothermic or endothermic?

a. $2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O(\ell) + 135\ \text{kcal}$
b. $N_2\,(g) + O_2\,(g) + 45\,\text{kcal} \rightarrow 2\,NO\,(g)$

Solution

No calculations are required to address this question. Just identify where the "heat" is in the chemical equation.

a. Because energy is released; this reaction is exothermic.
b. Because energy is absorbed; this reaction is endothermic.

? Exercise 1.6.1

If the bond energy for H-Cl is 431 kJ/mol. What is the overall bond energy of 2 moles of HCl?

Answer

Simply multiply the average bond energy of H-Cl by 2. This leaves you with 862 kJ (Table T3).

✓ Example 1.6.2: Generation of Hydrogen Iodide

What is the enthalpy change for this reaction and is it endothermic or exothermic?

$$\mathrm{H_2(g) + I_2(g) \rightarrow 2HI(g)}$$

Solution

First look at the equation and identify which bonds exist on in the reactants.

- one H-H bond and
- one I-I bond

Now do the same for the products

- two H-I bonds

Then identify the bond energies of these bonds from the table above:

- H-H bonds: 436 kJ/mol
- I-I bonds: 151 kJ/mol

The sum of enthalpies on the reaction side is:

436 kJ/mole + 151 kJ/mole = 587 kJ/mol.

This is how much energy is needed to break the bonds on the reactant side. Then we look at the bond formation which is on the product side:

- 2 mol H-I bonds: 297 kJ/mol

The sum of enthalpies on the product side is:

2 x 297 kJ/mol= 594 kJ/mol

This is how much energy is released when the bonds on the product side are formed. The net change of the reaction is therefore

587-594= -7 kJ/mol.

Since this is negative, the reaction is *exothermic*.

✓ Example 1.6.2: Decomposition of Water

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$\mathrm{2H_2O(g) \rightarrow 2H_2 + O_2(g)}$$

Is the reaction written above exothermic or endothermic? Explain.

Solution

The enthalpy change deals with breaking two mole of O-H bonds and the formation of 1 mole of O-O bonds and two moles of H-H bonds (Table T3).

- The sum of the energies required to break the bonds on the reactants side is 4 x 460 kJ/mol = 1840 kJ/mol.
- The sum of the energies released to form the bonds on the products side is
  - 2 moles of H-H bonds = 2 x 436.4 kJ/mol = 872.8 kJ/mol
  - 1 moles of O=O bond = 1 x 498.7 kJ/mil = 498.7 kJ/mol

which is an output (released) energy of 872.8 kJ/mol + 498.7 kJ/mol = 1371.5 kJ/mol.

Total energy difference is 1840 kJ/mol – 1371.5 kJ/mol = 469 kJ/mol, which indicates that the reaction is *endothermic* and that 469 kJ of heat is needed to be supplied to carry out this reaction.

This reaction is **end**othermic since it requires energy to create bonds.

Summary

Energy is released to generate bonds, which is why the enthalpy change for breaking bonds is positive. Energy is required to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is negative because the system is releasing energy when forming bond.

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CHAPTER OVERVIEW

2: Spontaneity, Entropy and Free Energy

2.1: Spontaneity

2.2: Entropy and the Second Law of Thermodynamics

2.3: The Molecular Interpretation of Entropy

2.4: Entropy Changes in Chemical Reactions

2.5: Gibbs Energy

2.6: Standard Thermodynamic Properties for Selected Substances

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2.1: Spontaneity

Skills to Develop

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur by force. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions and how relatively quickly or slowly that natural change proceeds. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **2.1.1**).

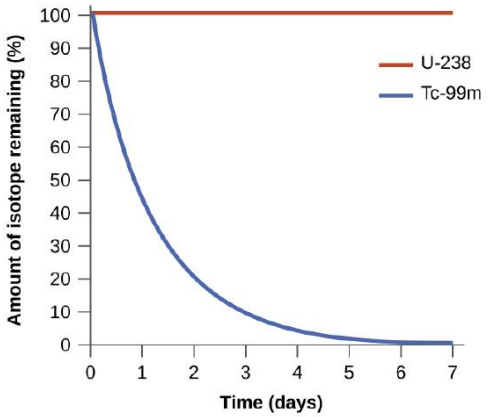


Figure **2.1.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure **2.1.2**).

$$\mathrm{C}_{(s,\ \text{diamond})} \longrightarrow \mathrm{C}_{(s,\ \text{graphite})} \tag{2.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed

"forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

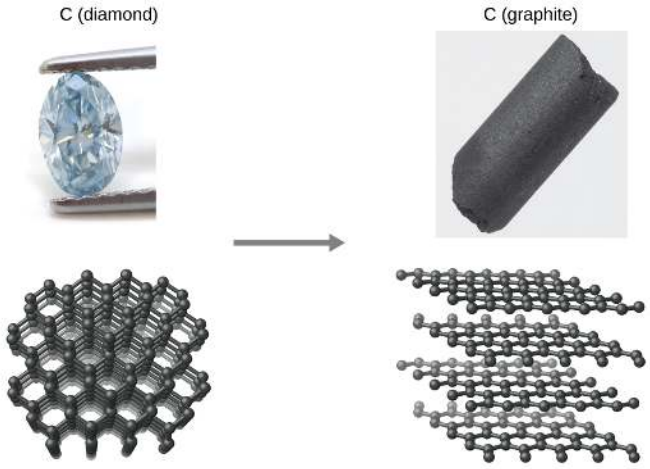


Figure 2.1.2:The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modificaton of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure 2.1.3). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V = 0 \quad (\text{P} = 0 \text{ in a vaccum}) \tag{2.1.2}$$

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.

$$\Delta U = q + w = 0 + 0 = 0 \tag{2.1.3}$$

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 process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

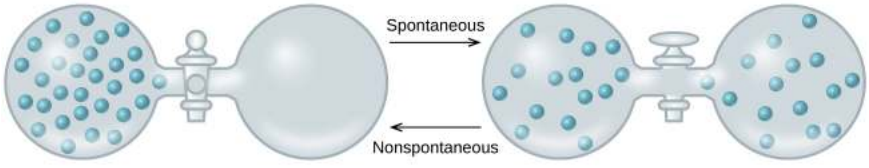


Figure 2.1.3:An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 2.1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \tag{2.1.4}$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 2.1.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 2.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

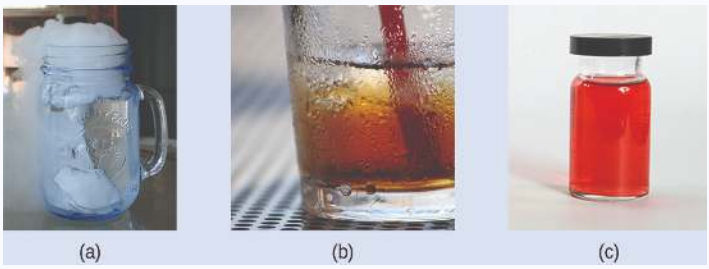


Figure 2.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)

1. (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.
2. (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 solid-to-gas transition.
3. (c) The process in question is dilution. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout.

Exercise 2.1.1

Describe how matter and/or energy is redistributed when you empty a canister of compressed air into a room.

Answer:

This is also a dilution process, analogous to example (c). It entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room.

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.

Glossary

nonspontaneous process

process that requires continual input of energy from an external source

spontaneous change

process that takes place without a continuous input of energy from an external source

Contributors

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2.2: Entropy and the Second Law of Thermodynamics

Learning Objectives

- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (U). Changes in the internal energy (ΔU) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned previously that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, by itself the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure **2.2.1**.

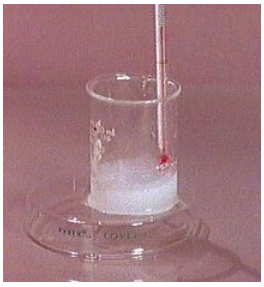


Figure **2.2.1**: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called **entropy (S)**, a thermodynamic property of all substances that is proportional to their degree of "disorder". In Chapter 13, we introduced the concept of entropy in relation to solution formation. Here we further explore the nature of this state function and define it mathematically.

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or microstates, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure **2.2.2**. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

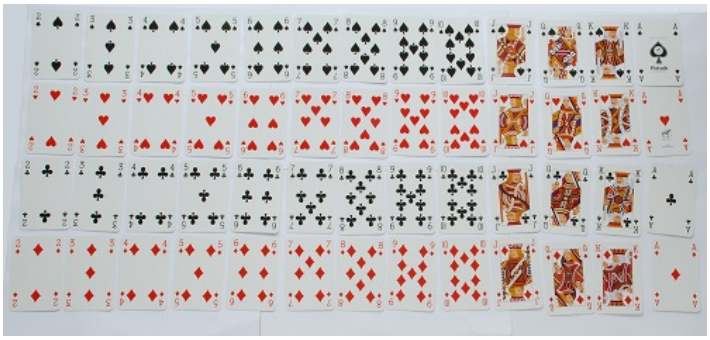


Figure **2.2.2**: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure **2.2.3**). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure **2.2.3**, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the most probable arrangement. The others are not impossible but simply less likely.

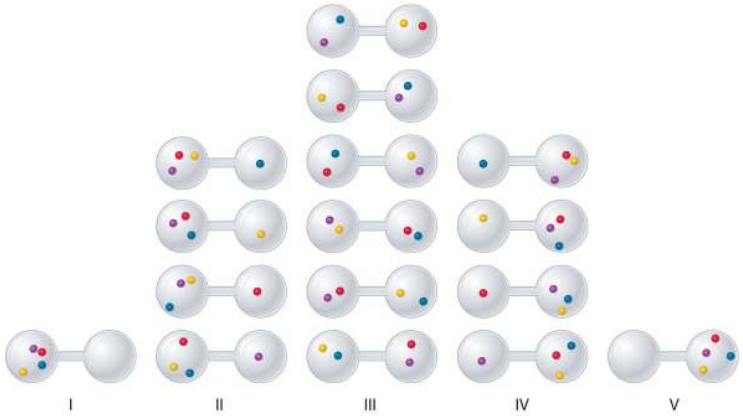


Figure **2.2.3**: The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume

There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is so improbable that it is likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23} molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately $\frac{2}{2.69 \times 10^{22}}$. The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are many equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

> Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure **2.2.4**, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors.

In the case of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

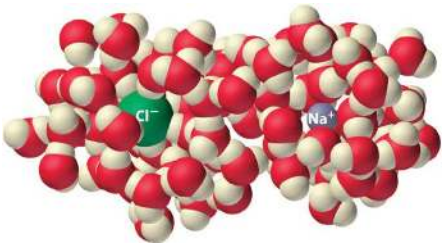


Figure **2.2.4**: The Effect of Solution Formation on Entropy

Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.

✔ Example 2.2.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
b. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

a. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.
b. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

? Exercise 2.2.1

Predict which substance in each pair has the higher entropy and justify your answer.

a. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
b. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer a

1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)

Answer a

a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

Video Solution

Reversible and Irreversible Changes

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, a reversible process can change direction at any time, whereas an irreversible process cannot. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = - P_{ext}\Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, $\Delta U = q + w$. Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{2.2.1}$$

> Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{rev} = T\Delta S \text{ and } \Delta S = \frac{q_{rev}}{T} \tag{2.2.2}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 2.2.1 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{2.2.3}$$

$$= T\Delta S - P\Delta V \tag{2.2.4}$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 2.2.2 and Equation 2.2.4, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 2.2.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings:

$$w_{rev} = -P\Delta V < 0.$$

According to Equation 2.2.4, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is

$$\Delta S_{surr} = -\frac{q_{rev}}{T}.$$

The corresponding change in entropy of the universe is then as follows:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ &= \frac{q_{\text{rev}}}{T} + \left(-\frac{q_{\text{rev}}}{T}\right) \\ &= 0\end{aligned}$$

Thus no change in ΔS_{univ} has occurred.

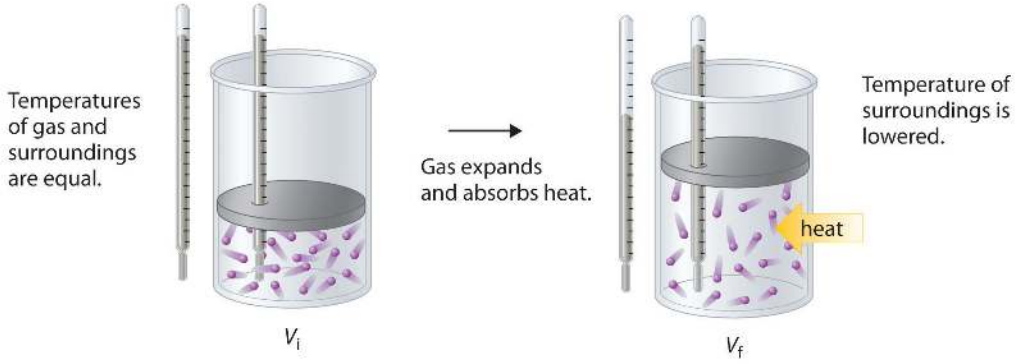


Figure **2.2.5**: Expansion of Gas at Constant Temperature

Temperatures of gas and surroundings are equal. Then the gas expands and absorbs heat. Temperature of the surroundings is then lowered.

In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure **2.2.6**. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 2.2.2, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fus}}}{T}$$

By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.

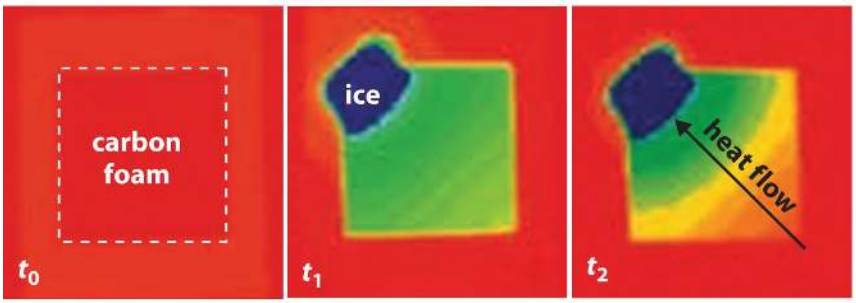


Figure **2.2.6**: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

In this case, ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol•K) = ΔS_{sys}. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = −(6.01 kJ/mol)/(273 K) = −22.0 J/(mol•K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0 \text{ J/(mol•K)} - 22.0 \text{ J/(mol•K)} = 0$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process.

The Second Law of Thermodynamics

The entropy of the universe **increases** during a spontaneous process. It also **increases** during an observable non-spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat (q > 0), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat (q < 0), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{univ} = \Delta S_{cold} + \Delta S_{hot} = \frac{q}{T_{cold}} + \left(-\frac{q}{T_{hot}}\right) \tag{2.2.5}$$

The numerators on the right side of Equation 2.2.5 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure **2.2.7**).



Figure **2.2.7**: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

Example 2.2.2: Tin Pest

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon was argued to have plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his soldiers' uniforms were made of tin and may have disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with ΔH = −2.1 kJ/mol at 13.2°C.

a. What is ΔS for this process?
b. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 2.2.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 2.2.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{rev}}{T} = \frac{(-2.1\ \text{kJ/mol})(1000\ \text{J/kJ})}{286.4\ \text{K}} = -7.3\ \text{J/(mol} \cdot \text{K)}$$

b. The fact that ΔS < 0 means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.



Video 2.2.1: *Time lapse tin pest reaction.*

Note: Whether failing buttons were indeed a contributing factor in the failure of the invasion remains disputed; critics of the theory point out that the tin used would have been quite impure and thus more tolerant of low temperatures. Laboratory tests provide evidence that the time required for unalloyed tin to develop significant tin pest damage at lowered temperatures is about 18 months, which is more than twice the length of Napoleon's Russian campaign. It is clear though that some of the regiments employed in the campaign had tin buttons and that the temperature reached sufficiently low values (at least -40 °C)

? Exercise 2.2.2

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

a. What is ΔS for this process?
b. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer a

1.09 J/(mol•K)

Answer b

S_α



Entropy: Entropy(opens in new window) [youtu.be]

Summary

For a given system, the greater the number of microstates, the higher the entropy. During a spontaneous process, the entropy of the universe increases.

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

A measure of the disorder of a system is its entropy (S), a state function whose value increases with an increase in the number of available microstates. A reversible process is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an irreversible process occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The second law of thermodynamics states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

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2.3: The Molecular Interpretation of Entropy

Learning Objectives

- To understand entropy from a molecular interpretation

As discussed previously, the second law of thermodynamics argues that all processes **must** increase the total entropy of the universe. However, the universe if often separated into the System and the Surroundings differing changes of entropy can be observed from a system level perspective. Many processes results in an increase in a *system's* entropy $\Delta S > 0$:

- Increasing the volume that a gas can occupy will increase the disorder of a gas
- Dissolving a solute into a solution will increase the entropy of the solute - typically resulting in an increase in the entropy of the system. (Note: the solvation of a solute can sometimes result in a significant *decrease* in the *solvent* entropy - leading to a *net decrease* in entropy of the *system*)
- Phase changes from solid to liquid, or liquid to gas, lead to an increase in the entropy of the system

Some processes result in a *decrease* in the entropy of a *system* $\Delta S < 0$:

- A gas molecule dissolved in a liquid is much more confined by neighboring molecules than when its in the gaseous state. Thus, the entropy of the gas molecule will decrease when it is dissolved in a liquid
- A phase change from a liquid to a solid (i.e. freezing), or from a gas to a liquid (i.e. condensation) results in an *decrease in the disorder* of the substance, and a *decrease in the entropy*
- A chemical reaction between gas molecules that results in *a net decrease* in the overall **number** of gas molecules will de*crease the disorder* of the system, and result in a *decrease in the entropy*

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \quad \Delta S < 0 \tag{2.3.1}$$

What is the molecular basis for the above observations for the change in entropy? Let's first consider the last example, the decrease in entropy associated with a decrease in the number of gas molecules for a chemical reaction

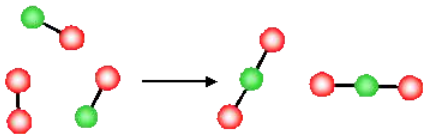


Figure 2.3.1: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

The product of this reaction (NO_2) involves *the formation of a new N-O bond* and the O atoms, originally in a separate O_2 molecule, *are now connected* to the NO molecule via a new $N-O$ bond.

- Since they are now physically bonded to the other molecule (forming a new, larger, single molecule) the O atoms have *less freedom* to move around
- The reaction has resulted in a loss of freedom of the atoms (O atoms)
- There is a reduction in the disorder of the system (i.e. due to the reduction in the degrees of freedom, the system is *more ordered* after the reaction). $\Delta S < 0$.

Molecular Degrees of Freedom

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 2.3.2).

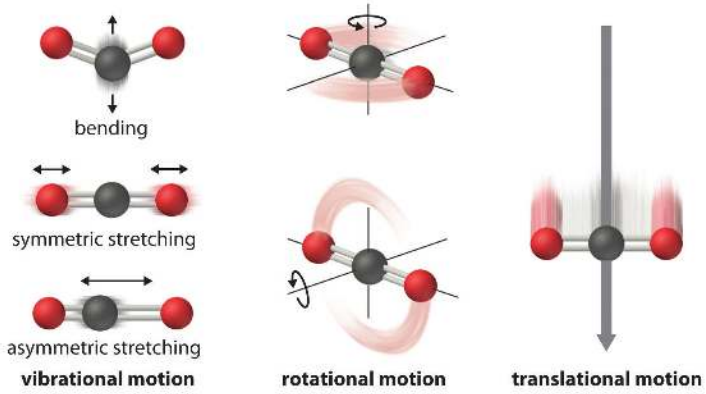


Figure **2.3.2**: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

- *Translational motion*. The entire molecule can move in some direction in three dimensions
- *Rotational motion*. The entire molecule can rotate around any axis, (even though it *may not actually change its position translationally*)
- *Vibrational motion*. The atoms within a molecule have certain freedom of movement relative to each other; this displacement can be periodic motion like the vibration of a tuning fork

These forms of molecular motion are ways in which molecules can store energy. The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy.

The Third Law of Thermodynamics

These forms of motion are ways in which the molecule can store energy. The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion (ignoring quantum effects). Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the *third law of thermodynamics*: the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.

The Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero (i.e. 0 Kelvin) is 0.

Since S = 0 corresponds to *perfect order*. The position of the atoms or molecules in the crystal would be perfectly defined

- As the temperature increases, the entropy of the atoms in the lattice increase
- Vibrational motions cause the atoms and molecules in the lattice to be less well ordered

The third law of thermodynamics has two important consequences: it defines the sign of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The area under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only relative terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those discussed previously.

Motion never stops at absolute zero!

From classical kinetic theory, all motions cease at absolute zero. However things are more complicated from the more advanced (and more accurate) quantum mechanics. The Heisenberg Uncertainly Principle of quantum mechanics argues that molecules, even at absolute zero, always always have motion. Nonetheless, this motion is often ignored in the introduction of the third law of thermodynamics (which is incorrect of course).

Continued heating of a Solid Lattice

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy (S°), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of S° are J/(mol·K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to S = 0 J/(mol·K)] and 298 K.

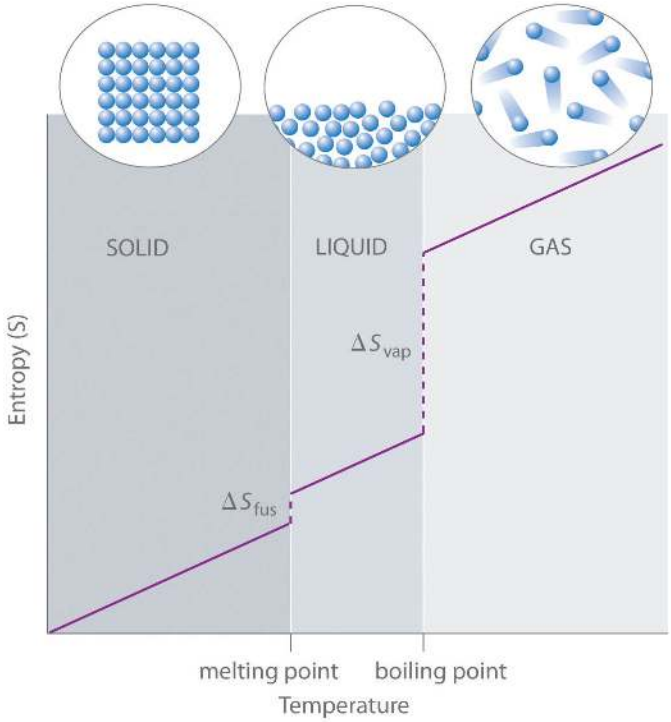


Figure **2.3.3**: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

As shown in Table **2.3.1**, for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol·K), whereas S° for water vapor is 188.8 J/(mol·K). Likewise, S° is 260.7 J/(mol·K) for gaseous I_2 and 116.1 J/(mol·K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure **2.3.2**, which is a generalized plot of the entropy of a substance versus temperature.

Table **2.3.1**: Standard Molar Entropy Values of Selected Substances at 25°C

Gases		Liquids		Solids	
Substance	*S° [J/(mol·K)]*	*Substance*	*S° [J/(mol·K)]*	*Substance*	*S° [J/(mol·K)]*
He	126.2	H_2O	70.0	C (diamond)	2.4
H_2	130.7	CH_3OH	126.8	C (graphite)	5.7
Ne	146.3	Br_2	152.2	LiF	35.7
Ar	154.8	CH_3CH_2OH	160.7	SiO_2 (quartz)	41.5
Kr	164.1	C_6H_6	173.4	Ca	41.6
Xe	169.7	CH_3COCl	200.8	Na	51.3
H_2O	188.8	C_6H_{12} (cyclohexane)	204.4	MgF_2	57.2
N_2	191.6	C_8H_{18} (isooctane)	329.3	K	64.7
O_2	205.2			NaCl	72.1
CO_2	213.8			KCl	82.6
I_2	260.7			I_2	116.1

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

A closer examination of Table **2.3.1** also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol·K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol·K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.



Entropy: Entropy(opens in new window) [youtu.be]

Summary

In general, the entropy is expected to *increase* for the following types of processes:

1. The melting of a solid to form a liquid

2. The vaporization of a liquid (or solid) to produce a gas
3. Chemical reactions that involve phase changes of **solid → liquid/gas**, or **liquid → gas**
4. Chemical reactions that result in an increase in the number of gaseous molecules
5. Any time the temperature of a substance is increased

Contributors and Attributions

- Mike Blaber (Florida State University)

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2.4: Entropy Changes in Chemical Reactions

Learning Objectives

- To calculate entropy changes for a chemical reaction

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter). Tragically, there is no comparable easy way to experimentally measure the change in entropy for a reaction. Suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation? Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at °0C at 1 atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)

$$\mathrm{H_2O\,(s)\ \rightarrow H_2O\,(l)} \tag{2.4.1}$$

- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
- Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

> *However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)*

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system. In fact, values for the "standard molar entropy" of a substance have units of J/mol K, the same units as for molar heat capacity.

Standard Molar Entropy, S^0

The entropy of a substance has an absolute value of 0 entropy at 0 K.

- **Standard molar entropies** are listed for a reference temperature (like 298 K) and 1 atm pressure (i.e. the entropy of a pure substance at 298 K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!) Standard molar entropy values are listed for a variety of substances in Table T2.
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298 K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike *enthalpies of formation*, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the *n*, and *m*, terms below are there to indicate that the coefficients must be accounted for):

$$\Delta S^0 = \sum_n nS^0(products) - \sum_m mS^0(reactants)$$

Example 2.4.1: Haber Process

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)\ \mhchemrightleftharpoons 2\,NH_3\,(g)}$$

At 298K as a standard temperature:

- $S^0(NH_3)$ = 192.5 J/mol K
- $S^0(H_2)$ = 130.6 J/mol K
- $S^0(N_2)$ = 191.5 J/mol K

Solution

From the balanced equation we can write the equation for ΔS^0 (the change in the standard molar entropy for the reaction):

$\Delta S^0 = 2*S^0(NH_3) - [S^0(N_2) + (3*S^0(H_2))]$

$\Delta S^0 = 2*192.5 - [191.5 + (3*130.6)]$

$\Delta S^0 = -198.3$ J/mol K

It would appear that the process results in a ***decrease*** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the $N_2(g)$ used to float around independently of the H_2 gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process!)

To calculate ΔS° for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example **2.4.2** illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

ΔS° for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate ΔH°.

Example 2.4.2: Combustion of Octane

Use the data in Table T2 to calculate ΔS° for the combustion reaction of liquid isooctane with O_2(g) to give CO_2(g) and H_2O(g) at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: ΔS°

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table T2. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain ΔS° for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$\mathrm{C_8H_{18}\,(l) + \tfrac{25}{2}\,O_2\,(g) \;\rightarrow 8\,CO_2\,(g) + 9\,H_2O\,(g)}$$

We calculate ΔS° for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= \sum mS^\circ(\text{products}) - \sum nS^\circ(\text{reactants})\\ &= [8S^\circ(\mathrm{CO_2}) + 9S^\circ(\mathrm{H_2O})] - [S^\circ(\mathrm{C_8H_{18}}) + \frac{25}{2}S^\circ(\mathrm{O_2})]\\ &= \{[8\text{ mol }\mathrm{CO_2} \times 213.8\text{ J/(mol}\cdot\text{K)}] + [9\text{ mol }\mathrm{H_2O} \times 188.8\text{ J/(mol}\cdot\text{K)}]\}\\ &\quad - \left\{[1\text{ mol }\mathrm{C_8H_{18}} \times 329.3\text{ J/(mol}\cdot\text{K)}] + \left[\frac{25}{2}\text{ mol }\mathrm{O_2} \times 205.2\text{ J/(mol}\cdot\text{K)}\right]\right\}\\ &= 515.3\text{ J/K}\end{aligned}$$

ΔS° is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

? Exercise 2.4.2

Use the data in Table T2 to calculate ΔS° for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer

−361.1 J/K



Calculating the Entropy of Reaction using S: Calculating the Entropy of Reaction using S(opens in new window) [youtu.be]

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2.5: Gibbs Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the standard free energy change for a process using standard free energies of formation for its reactants and products
- Calculate standard free energy change for a process using senthalpies 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 chemical reaction is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. A second challenge when working with a chemical reaction is that we need to take into account the mixing of the substances, an issue that does not occur when observing the phase change if a pure substance. 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 standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G^\circ_{\text{sys}} = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

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

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

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

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

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

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

$$\Delta G = -T\Delta S_{\text{univ}} \tag{2.5.1}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 2.5.1 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 2.5.1: 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)

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 that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical changes and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 2.5.1.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2.5.2}$$

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

Example 2.5.1: Evaluation of ΔG° for a Phase Change of a Pure Substance

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this physical change for a pure substance?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{2.5.3}$$

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

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ \tag{2.5.4}$$

From Tables T1 or T2, here are the data:

Data from Tables T1 or T2

Substance	ΔH_f° (kJ/mol)	S°_{298} (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\begin{aligned}
\Delta H^\circ &= \Delta H^\circ_{298} = \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l)) \\
&= [-241.82\ kJ - (-285.83)]\ kJ/mol \\
&= 44.01\ kJ/mol \\
\Delta S^\circ &= \Delta S^\circ_{298} = S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l)) \\
&= 188.8\ J/mol \cdot K - 70.0\ J/K \\
&= 118.8\ J/mol \cdot K
\end{aligned}$$

then use Equation 2.5.2:

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

Converting everything into kJ and combining at 298 K:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

$$= 44.01\ kJ/mol - (298\ K \times 118.8\ J/mol \cdot K) \times \frac{1\ kJ}{1000\ J}$$

$$44.01\ \text{kJ/mol} - 35.4\ \text{kJ/mol} = 8.6\ \text{kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous) at 298 K.

? Exercise 2.5.1: Evaluation of ΔG° for a Chemical Reaction

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the extent of this reaction at 298 K?

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

Answer

$\Delta G^\circ_{298} = 102.0\ \text{kJ/mol}$; the reaction is reactant-favored at equilibrium at 25 °C. There will be more $\mathrm{C_2H_6}(g)$ than $\mathrm{H_2}(g)$ and $\mathrm{C_2H_4}(g)$ at equilibrium

Free energy changes may also use the standard free energy of formation $(\Delta G^\circ_\mathrm{f})$, for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, $(\Delta G^\circ_\mathrm{f})$ is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\mathrm{A} + n\mathrm{B} \longrightarrow x\mathrm{C} + y\mathrm{D},$$

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

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{2.5.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \tag{2.5.6}$$

$$= [x\Delta G^\circ_\mathrm{f}(\mathrm{C}) + y\Delta G^\circ_\mathrm{f}(\mathrm{D})] - [m\Delta G^\circ_\mathrm{f}(\mathrm{A}) + n\Delta G^\circ_\mathrm{f}(\mathrm{B})]. \tag{2.5.7}$$

✔ Example 2.5.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

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

Calculate the standard free energy change at room temperature, ΔG°_{298}, using:

a. standard free energies of formation and
b. standard enthalpies of formation and standard entropies.

Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium?

Solution

The required data are available in Tables T1 or T2 and are shown here.

Required data for Tables T1 or T2

Compound	$\Delta G^\circ_\mathrm{f}$ (kJ/mol)	$\Delta H^\circ_\mathrm{f}$ (kJ/mol)	S°_{298} (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ_{298} &= \sum \nu GS^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta G^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\text{O}_2(g)\right] - 1\Delta G^\circ_{298}\text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ_{298} &= \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1\Delta H^\circ_{298}\text{HgO}(s,\text{ yellow}) \\ &= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol} \\ \Delta S^\circ_{298} &= \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1\Delta S^\circ_{298}\text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) = 107.4\text{ J/mol K}\end{aligned}$$

then we can use Equation \ref7} directly:

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

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 reactant-favored at equilibrium at room temperature.

? Exercise 2.5.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Tables T1 or T2). Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer

141.5 kJ/mol, reactant-favored at equilibrium

Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

Note

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

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

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

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

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

These four scenarios are summarized in Table 2.5.1

Table 2.5.1

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.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 2.5.3: 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 2.5.3

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 2.5.2. 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 ΔG^o < 0, K > 1, and the reaction will be product-favored at equilibrium. When ΔG^o > 0, K< 1, and the reaction is reactant-favored at equilibrium. When ΔG^o = 0, K =1, and the reaction will have roughly equal amounts of products and

reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

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

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

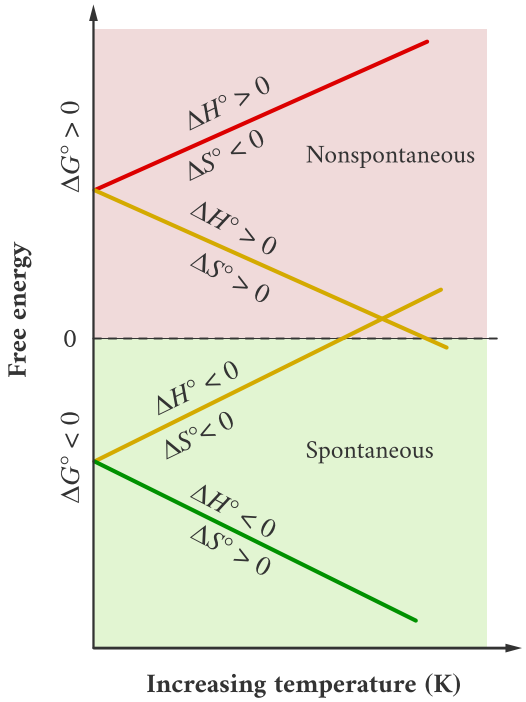


Figure 2.5.2: These plots show the variation in ΔGº with temperature for the four possible combinations of arithmetic sign for ΔHº and ΔSº. Note that in this graph of ΔGº, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

✔ Example 2.5.4: 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 2.5.4

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 finite 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 so 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, ΔG, is related to the standard free energy change, $\Delta G°$, according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{2.5.8}$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in Example 2.5.1.

✓ Example 2.5.5: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

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

$$2\,\mathrm{NH_3}(g) \longrightarrow 3\,\mathrm{H_2}(g) + \mathrm{N_2}(g) \quad \Delta G^\circ = 33.0\ \mathrm{kJ/mol}$$

Solution

Equation 2.5.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

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

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions. The reaction will proceed in the reverse direction to reach equilibrium.

Exercise 2.5.5

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 = −47 kJ; yes, the reaction proceeds in the forward direction, as written, to reach equilibrium.

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the Equation 2.5.8 may be written as

$$\underbrace{0 = \Delta G^\circ + RT\ln K}_{\text{at equilibrium}}$$

$$\Delta G^\circ = -RT\ln K \tag{2.5.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{2.5.10}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 2.5.1.

Table 2.5.1: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.
> 1	< 0	Products are more abundant at equilibrium.

Example 2.5.6: 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:

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

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

$$\begin{aligned}\Delta G^\circ = \Delta G^\circ_{298} &= [\Delta G^\circ_f(Ag^+(aq)) + \Delta G^\circ_f(Cl^-(aq))] - [\Delta G^\circ_f(AgCl(s))] \\ &= [77.1\ kJ/mol - 131.2\ kJ/mol] - [-109.8\ kJ/mol] \\ &= 55.7\ kJ/mol\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 2.5.10:

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

? Exercise 2.5.6: dissociation of dinitrogen tetroxide

Use the thermodynamic data provided in Tables T1 or T2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

Answer

K = 6.9

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 2.5.3). 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.

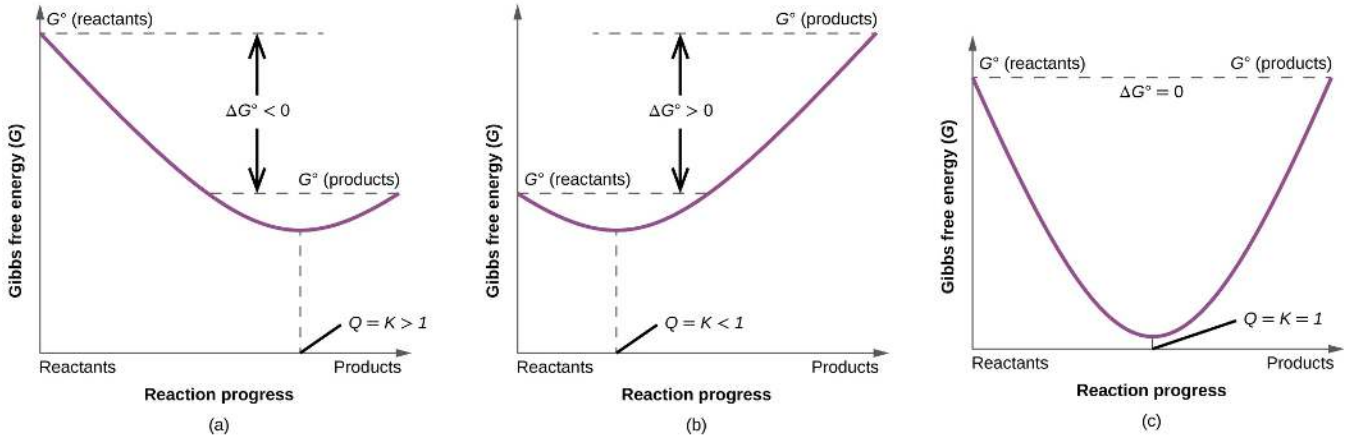


Figure 2.5.3: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note that reactions with K equal to exactly 1.000 are rare.

Summary

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 Δ*G* indicates that the process will proceed in the forward direction to reach equilibrium; a positive Δ*G* indicates that the process will proceed in the reverse direction to reach equilibrium ; and a Δ*G* of zero indicates that the system is at equilibrium. A negative value for Δ*G°* means that the reaction is product-favored at equilibrium. A positive value for Δ*G°* means that the reaction is reactant-favored at equilibrium. If Δ*G°* equals 0 (a rare occurrence), the reaction has roughly

equal amounts of reactants and products at equilibrium.A number of approaches to the computation of free energy changes are possible.

Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Glossary

Gibbs free energy change (G)

thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

standard free energy change ($\Delta G°$)

change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)

change in free energy accompanying the formation of one mole of substance from its elements in their standard states

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2.6: Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances

https://chem.libretexts.org/@go/page/440681

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
aluminum			
Al(s)	0	0	28.3
Al(g)	324.4	285.7	164.54
Al^{3+} (aq)	-531	-485	-321.7
Al_2O_3(s)	–1676	–1582	50.92
AlF_3(s)	–1510.4	–1425	66.5
$AlCl_3$(s)	–704.2	–628.8	110.67
$AlCl_3 \cdot 6H_2O$(s)	–2691.57	–2269.40	376.56
Al_2S_3(s)	–724.0	–492.4	116.9
$Al_2(SO_4)_3$(s)	–3445.06	–3506.61	239.32
antimony			
Sb(s)	0	0	45.69
Sb(g)	262.34	222.17	180.16
Sb_4O_6(s)	–1440.55	–1268.17	220.92
$SbCl_3$(g)	–313.8	–301.2	337.80
$SbCl_5$(g)	–394.34	–334.29	401.94
Sb_2S_3(s)	–174.89	–173.64	182.00
$SbCl_3$(s)	–382.17	–323.72	184.10
SbOCl(s)	–374.0	—	—
arsenic			
As(s)	0	0	35.1
As(g)	302.5	261.0	174.21
As_4(g)	143.9	92.4	314
As_4O_6(s)	–1313.94	–1152.52	214.22
As_2O_5(s)	–924.87	–782.41	105.44
$AsCl_3$(g)	–261.50	–248.95	327.06
As_2S_3(s)	–169.03	–168.62	163.59
AsH_3(g)	66.44	68.93	222.78
H_3AsO_4(s)	–906.3	—	—
barium			
Ba(s)	0	0	62.5
Ba(g)	180	146	170.24

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$\mathbf{Ba^{2+}}$ $\mathbf{(aq)}$	-537.6	-560.8	9.6
BaO(*s*)	–548.0	–520.3	72.1
$BaCl_2$(*s*)	–855.0	–806.7	123.7
$BaSO_4$(*s*)	–1473.2	–1362.3	132.2
beryllium			
Be(*s*)	0	0	9.50
Be(*g*)	324.3	286.6	136.27
BeO(*s*)	–609.4	–580.1	13.8
bismuth			
Bi(*s*)	0	0	56.74
Bi(*g*)	207.1	168.2	187.00
Bi_2O_3(*s*)	–573.88	–493.7	151.5
$BiCl_3$(*s*)	–379.07	–315.06	176.98
Bi_2S_3(*s*)	–143.1	–140.6	200.4
boron			
B(*s*)	0	0	5.86
B(*g*)	565.0	521.0	153.4
B_2O_3(*s*)	–1273.5	–1194.3	53.97
B_2H_6(*g*)	36.4	87.6	232.1
H_3BO_3(*s*)	–1094.33	–968.92	88.83
BF_3(*g*)	–1136.0	–1119.4	254.4
BCl_3(*g*)	–403.8	–388.7	290.1
$B_3N_3H_6$(*l*)	–540.99	–392.79	199.58
HBO_2(*s*)	–794.25	–723.41	37.66
bromine			
Br_2(*l*)	0	0	152.23
Br_2(*g*)	30.91	3.142	245.5
Br(*g*)	111.88	82.429	175.0
$\mathbf{Br^-}$ $\mathbf{(aq)}$	-120.9	-102.82	80.71
BrF_3(*g*)	–255.60	–229.45	292.42
HBr(*g*)	–36.3	–53.43	198.7
cadmium			

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Cd(s)	0	0	51.76
Cd(g)	112.01	77.41	167.75
Cd^{2+} (aq)	-75.90	-77.61	-73.2
CdO(s)	–258.2	–228.4	54.8
$CdCl_2$(s)	–391.5	–343.9	115.3
$CdSO_4$(s)	–933.3	–822.7	123.0
CdS(s)	–161.9	–156.5	64.9
calcium			
Ca(s)	0	0	41.6
Ca(g)	178.2	144.3	154.88
Ca^{2+} (aq)	-542.96	-553.04	-55.2
CaO(s)	–634.9	–603.3	38.1
$Ca(OH)_2$(s)	–985.2	–897.5	83.4
$CaSO_4$(s)	–1434.5	–1322.0	106.5
$CaSO_4 \cdot 2H_2O$(s)	–2022.63	–1797.45	194.14
$CaCO_3$(s) (calcite)	–1220.0	–1081.4	110.0
$CaSO_3 \cdot H_2O$(s)	–1752.68	–1555.19	184.10
carbon			
C(s) (graphite)	0	0	5.740
C(s) (diamond)	1.89	2.90	2.38
C(g)	716.681	671.2	158.1
CO(g)	–110.52	–137.15	197.7
CO_2(g)	–393.51	–394.36	213.8
CO_3^{2-} (aq)	-677.1	-527.8	-56.9
CH_4(g)	–74.6	–50.5	186.3
CH_3OH(l)	–239.2	–166.6	126.8
CH_3OH(g)	–201.0	–162.3	239.9
CCl_4(l)	–128.2	–62.5	214.4
CCl_4(g)	–95.7	–58.2	309.7
$CHCl_3$(l)	–134.1	–73.7	201.7
$CHCl_3$(g)	–103.14	–70.34	295.71
CS_2(l)	89.70	65.27	151.34

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	–84.0	–32.0	229.2
$CH_3CO_2H(l)$	–484.3	–389.9	159.8
$CH_3CO_2H(g)$	–434.84	–376.69	282.50
$C_2H_5OH(l)$	–277.6	–174.8	160.7
$C_2H_5OH(g)$	–234.8	–167.9	281.6
$HCO_3^-(aq)$	-691.11	-587.06	95
$C_3H_8(g)$	–103.8	–23.4	270.3
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	–124.2	–63.2	177.8
$CH_2Cl_2(g)$	–95.4	–65.90	270.2
$CH_3Cl(g)$	–81.9	–60.2	234.6
$C_2H_5Cl(l)$	–136.52	–59.31	190.79
$C_2H_5Cl(g)$	–112.17	–60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
cesium			
$Cs^+(aq)$	-248	-282.0	133
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$Cl^-(aq)$	-167.2	-131.2	56.5
$ClF(g)$	–54.48	–55.94	217.78
$ClF_3(g)$	–158.99	–118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	–92.307	–95.299	186.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$HClO_4(l)$	–40.58	—	—
chromium			
$Cr(s)$	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$\mathbf{CrO_4^{2-}}\,(aq)$	-881.2	-727.8	50.21
$\mathbf{Cr_2O_7^{2-}}\,(aq)$	-1490.3	-1301.1	261.9
$Cr_2O_3(s)$	–1139.7	–1058.1	81.2
$CrO_3(s)$	–589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	–1806.7	—	—
cobalt			
$Co(s)$	0	0	30.0
$\mathbf{Co^{2+}}\,(aq)$	-67.4	-51.5	-155
$\mathbf{Co^{3+}}\,(aq)$	92	134	-305.0
$CoO(s)$	–237.9	–214.2	52.97
$Co_3O_4(s)$	–910.02	–794.98	114.22
$Co(NO_3)_2(s)$	–420.5	—	—
copper			
$Cu(s)$	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
$\mathbf{Cu^{+}}\,(aq)$	51.9	50.2	-26
$\mathbf{Cu^{2+}}\,(aq)$	64.77	65.49	-99.6
$CuO(s)$	–157.3	–129.7	42.63
$Cu_2O(s)$	–168.6	–146.0	93.14
$CuS(s)$	–53.1	–53.6	66.5
$Cu_2S(s)$	–79.5	–86.2	120.9
$CuSO_4(s)$	–771.36	–662.2	109.2
$Cu(NO_3)_2(s)$	–302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
$F(g)$	79.4	62.3	158.8
$\mathbf{F^{-}}\,(aq)$	-332.6	-278.8	-13.8
$F_2O(g)$	24.7	41.9	247.43

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
HF(g)	–273.3	–275.4	173.8
hydrogen			
H_2(g)	0	0	130.7
H(g)	217.97	203.26	114.7
H^+ (aq)	0	0	0
OH^- (aq)	-230.0	-157.2	-10.75
H_3O^+ (aq)	-285.8		69.91
H_2O(l)	–285.83	–237.1	70.0
H_2O(g)	–241.82	–228.59	188.8
H_2O_2(l)	–187.78	–120.35	109.6
H_2O_2(g)	–136.3	–105.6	232.7
HF(g)	–273.3	–275.4	173.8
HCl(g)	–92.307	–95.299	186.9
HBr(g)	–36.3	–53.43	198.7
HI(g)	26.48	1.70	206.59
H_2S(g)	–20.6	–33.4	205.8
H_2Se(g)	29.7	15.9	219.0
iodine			
I_2(s)	0	0	116.14
I_2(g)	62.438	19.3	260.7
I(g)	106.84	70.2	180.8
I^- (aq)	-55.19	-51.57	11.13
IF(g)	95.65	–118.49	236.06
ICl(g)	17.78	–5.44	247.44
IBr(g)	40.84	3.72	258.66
IF_7(g)	–943.91	–818.39	346.44
HI(g)	26.48	1.70	206.59
iron			
Fe(s)	0	0	27.3
Fe(g)	416.3	370.7	180.5
Fe^{2+} (aq)	-89.1	-78.90	-137.7
Fe^{3+} (aq)	-48.5	-4.7	-315.9

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$Fe_2O_3(s)$	–824.2	–742.2	87.40
$Fe_3O_4(s)$	–1118.4	–1015.4	146.4
$Fe(CO)_5(l)$	–774.04	–705.42	338.07
$Fe(CO)_5(g)$	–733.87	–697.26	445.18
$FeCl_2(s)$	–341.79	–302.30	117.95
$FeCl_3(s)$	–399.49	–334.00	142.3
$FeO(s)$	–272.0	–255.2	60.75
$Fe(OH)_2(s)$	–569.0	–486.5	88.
$Fe(OH)_3(s)$	–823.0	–696.5	106.7
$FeS(s)$	–100.0	–100.4	60.29
$Fe_3C(s)$	25.10	20.08	104.60
lead			
$Pb(s)$	0	0	64.81
$Pb(g)$	195.2	162.	175.4
$\mathbf{Pb^{2+}}$ $\boldsymbol{(aq)}$	-1.7	-24.43	10.5
PbO(s) (yellow)	–217.32	–187.89	68.70
PbO(s) (red)	–218.99	–188.93	66.5
$Pb(OH)_2(s)$	–515.9	—	—
$PbS(s)$	–100.4	–98.7	91.2
$Pb(NO_3)_2(s)$	–451.9	—	—
$PbO_2(s)$	–277.4	–217.3	68.6
$PbCl_2(s)$	–359.4	–314.1	136.0
lithium			
$Li(s)$	0	0	29.1
$Li(g)$	159.3	126.6	138.8
$\mathbf{Li^+}$ $\boldsymbol{(aq)}$	-278.5	-293.3	13.4
$LiH(s)$	–90.5	–68.3	20.0
$Li(OH)(s)$	–487.5	–441.5	42.8
$LiF(s)$	–616.0	–587.5	35.7
$Li_2CO_3(s)$	–1216.04	–1132.19	90.17
magnesium			
$\mathbf{Mg^{2+}}$ $\boldsymbol{(aq)}$	-466.9	-454.8	-138.1

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
manganese			
Mn(*s*)	0	0	32.0
Mn(*g*)	280.7	238.5	173.7
$\mathbf{Mn^{2+}}$ (*aq*)	-220.8	-228.1	-73.6
MnO(*s*)	–385.2	–362.9	59.71
MnO_2(*s*)	–520.03	–465.1	53.05
Mn_2O_3(*s*)	–958.97	–881.15	110.46
Mn_3O_4(*s*)	–1378.83	–1283.23	155.64
$\mathbf{MnO_4^-}$ (*aq*)	-541.4	-447.2	191.2
$\mathbf{MnO_4^{2-}}$ (*aq*)	-653.0	-500.7	59
mercury			
Hg(*l*)	0	0	75.9
Hg(*g*)	61.4	31.8	175.0
$\mathbf{Hg^{2+}}$ (*aq*)		164.8	
$\mathbf{Hg_2^{2+}}$ (*aq*)	172.4	153.9	84.5
HgO(*s*) (red)	–90.83	–58.5	70.29
HgO(*s*) (yellow)	–90.46	–58.43	71.13
$HgCl_2$(*s*)	–224.3	–178.6	146.0
Hg_2Cl_2(*s*)	–265.4	–210.7	191.6
HgS(*s*) (red)	–58.16	–50.6	82.4
HgS(*s*) (black)	–53.56	–47.70	88.28
$HgSO_4$(*s*)	–707.51	–594.13	0.00
nitrogen			
N_2(*g*)	0	0	191.6
N(*g*)	472.704	455.5	153.3
NO(*g*)	90.25	87.6	210.8
NO_2(*g*)	33.2	51.30	240.1
N_2O(*g*)	81.6	103.7	220.0
N_2O_3(*g*)	83.72	139.41	312.17
$\mathbf{NO_3^-}$ (*aq*)	-205.0	-108.7	146.4
N_2O_4(*g*)	11.1	99.8	304.4
N_2O_5(*g*)	11.3	115.1	355.7

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$NH_3(g)$	–45.9	–16.5	192.8
$\mathbf{NH_4^+}$ $\mathbf{(aq)}$	-132.5	-79.31	113.4
$N_2H_4(l)$	50.63	149.43	121.21
$N_2H_4(g)$	95.4	159.4	238.5
$NH_4NO_3(s)$	–365.56	–183.87	151.08
$NH_4Cl(s)$	–314.43	–202.87	94.6
$NH_4Br(s)$	–270.8	–175.2	113.0
$NH_4I(s)$	–201.4	–112.5	117.0
$NH_4NO_2(s)$	–256.5	—	—
$HNO_3(l)$	–174.1	–80.7	155.6
$HNO_3(g)$	–133.9	–73.5	266.9
oxygen			
$O_2(g)$	0	0	205.2
$O(g)$	249.17	231.7	161.1
$O_3(g)$	142.7	163.2	238.9
phosphorus			
$P_4(s)$	0	0	164.4
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	–287.0	–267.8	311.78
$PCl_5(g)$	–374.9	–305.0	364.4
$P_4O_6(s)$	–1640.1	—	—
$P_4O_{10}(s)$	–2984.0	–2697.0	228.86
$\mathbf{PO_4^{3-}}$ $\mathbf{(aq)}$	-1277	-1019	-222
$HPO_3(s)$	–948.5	—	—
$\mathbf{HPO_4^{2-}}$ $\mathbf{(aq)}$	-1292.1	-1089.3	-33
$\mathbf{H_2PO_4^-}$ $\mathbf{(aq)}$	-1296.3	-1130.4	90.4
$H_3PO_2(s)$	–604.6	—	—
$H_3PO_3(s)$	–964.4	—	—
$H_3PO_4(s)$	–1279.0	–1119.1	110.50
$H_3PO_4(l)$	–1266.9	–1124.3	110.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$H_4P_2O_7(s)$	–2241.0	—	—
$POCl_3(l)$	–597.1	–520.8	222.5
$POCl_3(g)$	–558.5	–512.9	325.5
potassium			
$K(s)$	0	0	64.7
$K(g)$	89.0	60.5	160.3
$K^+(aq)$	-252.4	-283.3	102.5
$KF(s)$	–576.27	–537.75	66.57
$KCl(s)$	–436.5	–408.5	82.6
rubidium			
$Rb^+(aq)$	-246	-282.2	124
silicon			
$Si(s)$	0	0	18.8
$Si(g)$	450.0	405.5	168.0
$SiO_2(s)$	–910.7	–856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6
$H_2SiO_3(s)$	–1188.67	–1092.44	133.89
$H_4SiO_4(s)$	–1481.14	–1333.02	192.46
$SiF_4(g)$	–1615.0	–1572.8	282.8
$SiCl_4(l)$	–687.0	–619.8	239.7
$SiCl_4(g)$	–662.75	–622.58	330.62
SiC(*s, beta cubic*)	–73.22	–70.71	16.61
SiC(*s, alpha hexagonal*)	–71.55	–69.04	16.48
silver			
$Ag(s)$	0	0	42.55
$Ag(g)$	284.9	246.0	172.89
$Ag^+(aq)$	105.6	77.11	72.68
$Ag_2O(s)$	–31.05	–11.20	121.3
$AgCl(s)$	–127.0	–109.8	96.3
$Ag_2S(s)$	–32.6	–40.7	144.0
sodium			
$Na(s)$	0	0	51.3

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
Na(g)	107.5	77.0	153.7
$\mathbf{Na^+}$ $\boldsymbol{(aq)}$	-240.1	-261.9	59
$Na_2O(s)$	–414.2	–375.5	75.1
NaCl(s)	–411.2	–384.1	72.1
strontium			
$\mathbf{Sr^{2+}}$ $\boldsymbol{(aq)}$	-545.8	-557.3	-32.6
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
S(g)	278.81	238.25	167.82
$\mathbf{S^{2-}}$ $\boldsymbol{(aq)}$	41.8	83.7	22
$SO_2(g)$	–296.83	–300.1	248.2
$SO_3(g)$	–395.72	–371.06	256.76
$\mathbf{SO_4^{2-}}$ $\boldsymbol{(aq)}$	-909.3	-744.5	20.1
$\mathbf{S_2O_3^{2-}}$ $\boldsymbol{(aq)}$	-648.5	-522.5	67
$H_2S(g)$	–20.6	–33.4	205.8
$\mathbf{HS^-}$ $\boldsymbol{(aq)}$	-17.7	12.6	61.1
$H_2SO_4(l)$	–813.989	690.00	156.90
$\mathbf{HSO_4^-}$ $\boldsymbol{(aq)}$	-885.75	-752.87	126.9
$H_2S_2O_7(s)$	–1273.6	—	—
$SF_4(g)$	–728.43	–684.84	291.12
$SF_6(g)$	–1220.5	–1116.5	291.5
$SCl_2(l)$	–50	—	—
$SCl_2(g)$	–19.7	—	—
$S_2Cl_2(l)$	–59.4	—	—
$S_2Cl_2(g)$	–19.50	–29.25	319.45
$SOCl_2(g)$	–212.55	–198.32	309.66
$SOCl_2(l)$	–245.6	—	—
$SO_2Cl_2(l)$	–394.1	—	—
SO_2Cl_2(g)	–354.80	–310.45	311.83
tin			
Sn(s)	0	0	51.2
Sn(g)	301.2	266.2	168.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
SnO(*s*)	–285.8	–256.9	56.5
SnO_2(*s*)	–577.6	–515.8	49.0
$SnCl_4$(*l*)	–511.3	–440.1	258.6
$SnCl_4$(*g*)	–471.5	–432.2	365.8
titanium			
Ti(*s*)	0	0	30.7
Ti(*g*)	473.0	428.4	180.3
TiO_2(*s*)	–944.0	–888.8	50.6
$TiCl_4$(*l*)	–804.2	–737.2	252.4
$TiCl_4$(*g*)	–763.2	–726.3	353.2
tungsten			
W(*s*)	0	0	32.6
W(*g*)	849.4	807.1	174.0
WO_3(*s*)	–842.9	–764.0	75.9
zinc			
Zn(*s*)	0	0	41.6
Zn(*g*)	130.73	95.14	160.98
Zn^{2+} (*aq*)	-153.9	-147.1	-112.1
ZnO(*s*)	–350.5	–320.5	43.7
$ZnCl_2$(*s*)	–415.1	–369.43	111.5
ZnS(*s*)	–206.0	–201.3	57.7
$ZnSO_4$(*s*)	–982.8	–871.5	110.5
$ZnCO_3$(*s*)	–812.78	–731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	–898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	–896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	–837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	–2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	–874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	–877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	–689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	–681.2	—	—

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol$^-$)	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
$[Co(en)_2Cl_2]Cl$, *trans*	–677.4	—	—
$[Co(en)_3](ClO_4)_3$	–762.7	—	—
$[Co(en)_3]Br_2$	–595.8	—	—
$[Co(en)_3]I_2$	–475.3	—	—
$[Co(en)_3]I_3$	–519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	–1034.7	–221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	–1088.7	–412.9	331
$[Co(NH_3)_6](NO_3)_3$	–1282.0	–524.5	448
$[Co(NH_3)_5Cl]Cl_2$	–1017.1	–582.5	366.1
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

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CHAPTER OVERVIEW

3: Reaction Kinetics

3.1: Chemical Reaction Rates
3.2: Factors Affecting Reaction Rates
3.3: Rate Laws
3.4: Integrated Rate Laws
3.5: First-Order Reactions
3.6: Second-Order Reactions
3.7: Zero-Order Reactions
3.8: Pseudo-1st-order reactions
3.9: Reaction Mechanisms
3.10: The Collision Theory
3.11: Arrhenius Equation
3.12: Kinetics of Catalysis

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3.1: Chemical Reaction Rates

Learning Objectives

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

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, $[H_2O_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure 3.1.1 provides an example of data collected during the decomposition of H_2O_2.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
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	−0.0103
24.00	0.0625			

Figure 3.1.1: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\ \text{mol/L} - 1.000\ \text{mol/L})}{(6.00\ \text{h} - 0.00\ \text{h})} = 0.0833\ \text{mol L}^{-1}\ \text{h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625\ \text{mol/L} - 0.125\ \text{mol/L})}{(24.00\ \text{h} - 18.00\ \text{h})} = 0.0104\ \text{mol L}^{-1}\ \text{h}^{-1}$$

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. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 3.1.2). We can use calculus to evaluating the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

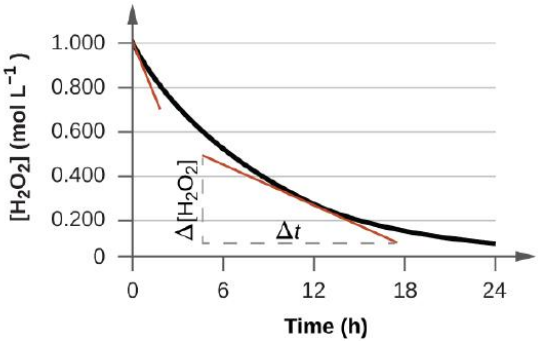


Figure 3.1.1: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" at that particular time).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 3.1.2). 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:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2 \tag{3.1.1}$$

$$2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2 \tag{3.1.2}$$

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Equation 3.1.1 depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine (Equation 3.1.2), which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

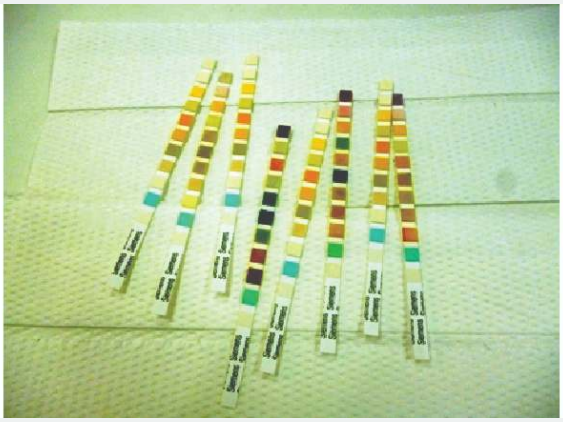


Figure 3.1.2: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

3.1.1: Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction. Consider the reaction represented by the following equation:

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

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to related reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta \text{mol NH}_3}{\Delta t} \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2}\frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Similarly, the rate of formation of $\mathrm{H_2}$ is three times the rate of formation of $\mathrm{N_2}$ because three moles of $\mathrm{H_2}$ form during the time required for the formation of one mole of $\mathrm{N_2}$:

$$\frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Figure 3.1.3 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at t = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\text{s}}{9.71 \times 10^{-6}\ M/\text{s}} \approx 3$$

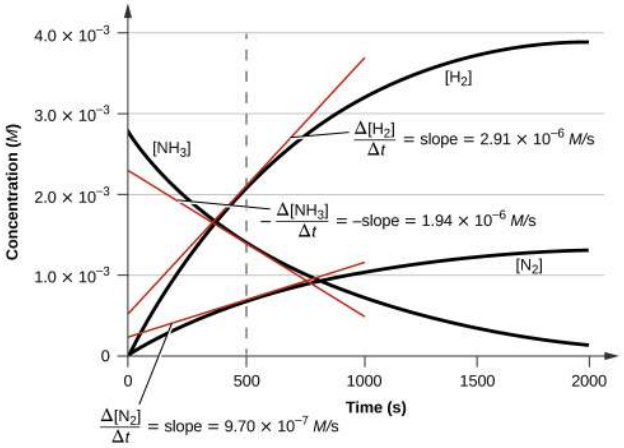


Figure 3.1.3: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

Example 3.1.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

Exercise 3.1.1

The rate of formation of Br_2 is 6.0 × 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5\,Br^- + BrO_3^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

Example 3.1.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 3.1.3 shows the rate of the decomposition of H_2O_2 over time:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20 × 10^{-2} mol/L/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

Using the stoichiometry of the reaction, we may determine that:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\ \text{mol}\ \text{L}^{-1}\ \text{h}^{-1}$$

Exercise 3.1.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10 × 10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05 × 10^{-6} mol/L/s, N_2 and 3.15 × 10^{-6} mol/L/s, H_2.

Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

Glossary

average rate
rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

initial rate
instantaneous rate of a chemical reaction at t = 0 s (immediately after the reaction has begun)

instantaneous rate
rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

rate of reaction
measure of the speed at which a chemical reaction takes place

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

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3.2: Factors Affecting Reaction Rates

Learning Objectives

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

3.2.1: The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

3.2.2: The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure **3.2.1**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure **3.2.1**: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area: 2Fe(s) + 6HCl(aq) ⟶ 2FeCl3(aq) + 3H2(g). (surfaceb) An iron nail reacts more slowly.

This figure shows two photos labeled (a) and (b). Photo (a) shows the bottom of a test tube. The test tube is filled with a dark gas, and there is a dark substance and bubbles in the bottom. Photo (b) shows a rod and bubbles in a test tube similar to photo (a), but the gas in the test tube is not as dark.



Video* 3.2.1: The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

3.2.3: Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

3.2.4: Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($\mathbf{CaCO_3}$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure **3.2.2**). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathbf{SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)}} \tag{3.2.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathbf{CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}} \tag{3.2.2}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

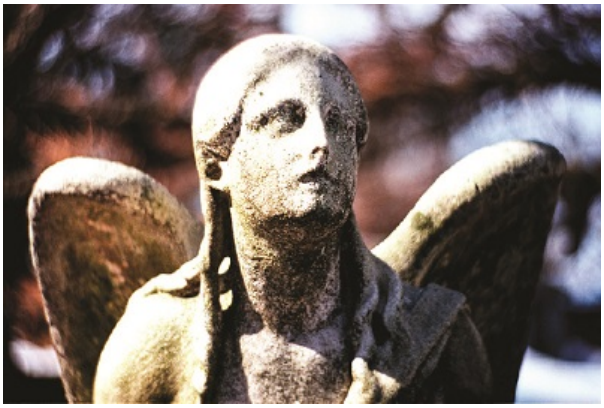


Figure **3.2.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III).

A photograph is shown of an angel statue. While some details of the statue, including facial features, are present, effects of weathering appear to be diminishing these features.



***Video* 3.2.2**: *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

3.2.5: The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure **3.2.3**). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

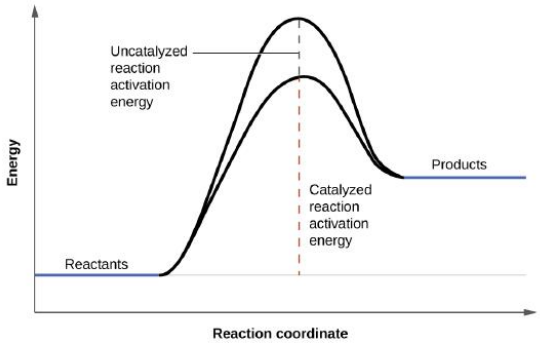


Figure **3.2.3**: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

A graph is shown with the label, "Reaction coordinate," on the x-axis. The x-axis is depicted as an arrow. The y-axis is also an arrow and is labeled, "Energy." There is a horizontal line that runs the width of the graph and appears just above the x-axis. A segment of this line is blue and is labeled, "Reactants." From the right end of this line segment, a solid black, concave down curve is shown which reaches the level just below the end of the y-axis. The curve ends at another short, blue line labeled, "Products." The "Products" line appears at a higher level than the "Reactants" line. An arrow extends from the horizontal line to the apex of the curve. The arrow is labeled, "Uncatalyzed reaction activation energy." A second, black concave down curve is shown. This curve also meets the reactants and products blue line segments, but only extends to about two-thirds the height of the initial curve. From the horizontal line is another arrow pointing to the apex of the second curve. This arrow is labeled, "Catalyzed reaction activation energy."

> *Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.*

Summary

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Glossary

catalyst

substance that increases the rate of a reaction without itself being consumed by the reaction

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3.3: Rate Laws

Learning Objectives

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. Rate laws or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

$$\text{rate} = k[A]^m[B]^n[C]^p \ldots$$

in which [*A*], [*B*], and [*C*] represent the molar concentrations of reactants, and *k* is the rate constant, which is specific for a particular reaction at a particular temperature. The exponents *m*, *n*, and *p* are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant *k* and the exponents *m*, *n*, and *p* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the concentration of *A*, *B*, or *C*, but it does vary with temperature and surface area.

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the reaction order. Consider a reaction for which the rate law is:

$$\text{rate} = k[A]^m[B]^n$$

If the exponent *m* is 1, the reaction is first order with respect to *A*. If *m* is 2, the reaction is second order with respect to *A*. If *n* is 1, the reaction is first order in *B*. If *n* is 2, the reaction is second order in *B*. If *m* or *n* is zero, the reaction is zero order in *A* or *B*, respectively, and the rate of the reaction is not affected by the concentration of that reactant. The overall reaction order is the sum of the orders with respect to each reactant. If *m* = 1 and *n* = 1, the overall order of the reaction is second order (*m* + *n* = 1 + 1 = 2).

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 3.3.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

The reaction is second order in NO_2; thus *m* = 2. The reaction is zero order in CO; thus *n* = 0. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 3.3.1A

The rate law for the reaction:

$$H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

has been experimentally determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2;
- order in H_2 = 1;
- overall order = 3

Exercise 3.3.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1;
- order in $CH_3CH_2OCOCH_3$ = 0;
- overall order = 1

It is sometimes helpful to use a more explicit algebraic method, often referred to as the method of initial rates, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

Example 3.3.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 3.3.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

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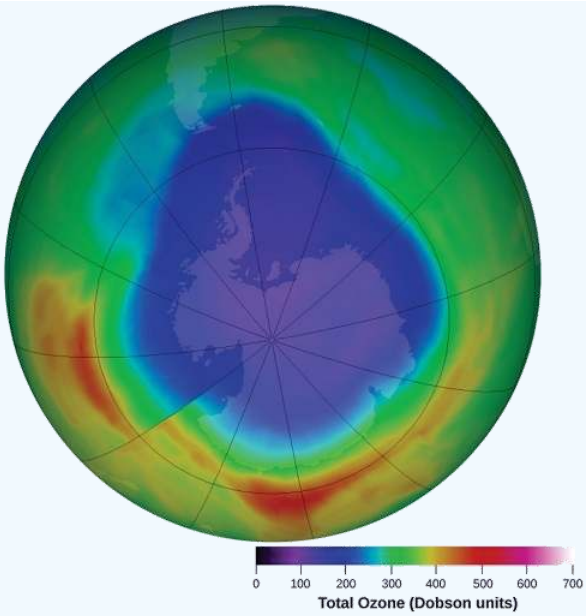


Figure 3.3.1: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

A view of Earth's southern hemisphere is shown. A nearly circular region of approximately half the diameter of the image is shown in shades of purple, with Antarctica appearing in a slightly lighter color than the surrounding ocean areas. Immediately outside this region is a narrow bright blue zone followed by a bright green zone. In the top half of the figure, the purple region extends slightly outward from the circle and the blue zone extends more outward to the right of the center as compared to the lower half of the image. In the upper half of the image, the majority of the space outside the purple region is shaded green, with a few small strips of interspersed blue regions. The lower half however shows the majority of the space outside the central purple zone in yellow, orange, and red. The red zones appear in the lower central and left regions outside the purple zone. To the lower right of this image is a color scale that is labeled "Total Ozone (Dobsone units)." This scale begins at 0 and increases by 100's up to 700. At the left end of the scale, the value 0 shows a very deep purple color, 100 is indigo, 200 is blue, 300 is green, 400 is a yellow-orange, 500 is red, 600 is pink, and 700 is white.

$$\mathrm{NO}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	$[\mathrm{NO}]$ (mol/L)	$[\mathrm{O_3}]$ (mol/L)	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}$ $(\mathrm{mol\ L^{-1}\ s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{O_3}]^n$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of* m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.
2. *Determine the value of* n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

3. *Determine the value of* k *from one set of concentrations and the corresponding rate*.

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \text{mol L}^{-1})(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

The large value of *k* tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Exercise 3.3.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	**[CH_3CHO] (mol/L)**	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ **(mol L^{-1} s^{-1})**
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

rate $= k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

Example 3.3.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{NOCl}(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{NO}]}{2\Delta t}$ (mol L^{-1} s^{-1})
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in Example 3.3.2, we can approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, we will use a different approach to determine the values of *m* and *n*:

Determine the value of m *from the data in which [NO] varies and [Cl_2] is constant.* We can write the ratios with the subscripts *x* and *y* to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m[\text{Cl}_2]_x^n}{k[\text{NO}]_y^m[\text{Cl}_2]_y^n}$$

Using the third trial and the first trial, in which [Cl_2] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

We can use natural logs to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)\frac{\ln(2.25)}{\ln(1.5)} \qquad = m2 = m$$

We can confirm the result easily, since:

$$1.5^2 = 2.25$$

- *Determine the value of* n *from data in which [Cl_2] varies and [NO] is constant.*

  $$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

  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:

  $$\text{Rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2]$$

- *Determine the numerical value of the rate constant* k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for *k* are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be $mol^{-2}\ L^2/s$ so that the rate is in terms of mol/L/s.

  To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

  $$0.00300\ \text{mol L}^{-1}\ \text{s}^{-1} = k(0.10\ \text{mol L}^{-1})^2(0.10\ \text{mol L}^{-1})^1$$
  $$k = 3.0\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

Exercise 3.3.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\mathrm{OCl^-}(aq) + \mathrm{I^-}(aq) \longrightarrow \mathrm{OI^-}(aq) + \mathrm{Cl^-}(aq)$$

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:

$$\text{rate} = k[\mathrm{OCl^-}]^2[\mathrm{I^-}]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 \text{ mol}^{-2}\text{ L}^2\text{ s}^{-1}$$

3.3.1: 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:

$$\mathrm{NO_2} + \mathrm{CO} \longrightarrow \mathrm{NO} + \mathrm{CO_2} \quad \text{rate} = k[\mathrm{NO_2}]^2$$

$$\mathrm{CH_3CHO} \longrightarrow \mathrm{CH_4} + \mathrm{CO} \quad \text{rate} = k[\mathrm{CH_3CHO}]^2$$

$$2\,\mathrm{N_2O_5} \longrightarrow 2\,\mathrm{NO_2} + \mathrm{O_2} \quad \text{rate} = k[\mathrm{N_2O_5}]$$

$$2\,\mathrm{NO_2} + \mathrm{F_2} \longrightarrow 2\,\mathrm{NO_2F} \quad \text{rate} = k[\mathrm{NO_2}][\mathrm{F_2}]$$

$$2\,\mathrm{NO_2Cl} \longrightarrow 2\,\mathrm{NO_2} + \mathrm{Cl_2} \quad \text{rate} = k[\mathrm{NO_2Cl}]$$

> *It is important to note that rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant *k*. In Example 3.3.2, a second-order reaction, we found the units for *k* to be $\mathrm{L\ mol^{-1}\ s^{-1}}$, whereas in Example 3.3.3, a third order reaction, we found the units for *k* to be $\mathrm{mol^{-2}\ L^2/s}$. More generally speaking, the units for the rate constant for a reaction of order $(m+n)$ are $\mathrm{mol}^{1-(m+n)}\mathrm{L}^{(m+n)-1}\mathrm{s}^{-1}$. Table 3.3.1 summarizes the rate constant units for common reaction orders.

Table 3.3.1: Rate Constants for Common Reaction Orders

Reaction Order	Units of *k*
$(m+n)$	$\mathrm{mol}^{1-(m+n)}\,\mathrm{L}^{(m+n)-1}\,\mathrm{s}^{-1}$
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$\mathrm{mol}^{-2}\,\mathrm{L}^2\,\mathrm{s}^{-1}$

Note that the units in the table can also be expressed in terms of molarity (*M*) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Summary

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Glossary

method of initial rates
use of a more explicit algebraic method to determine the orders in a rate law

overall reaction order
sum of the reaction orders for each substance represented in the rate law

rate constant (*k*)
proportionality constant in the relationship between reaction rate and concentrations of reactants

rate law
(also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

reaction order
value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

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3.4: Integrated Rate Laws

Learning Objectives

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws we have seen thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called integrated rate laws. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

3.4.1: First-Order Reactions

An equation relating the rate constant k to the initial concentration $[A]_0$ and the concentration $[A]_t$ present after any given time t can be derived for a first-order reaction and shown to be:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

or alternatively

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

or

$$[A] = [A]_0 e^{-kt}$$

Example 3.4.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2×10^{-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

We use the integrated form of the rate law to answer questions regarding time:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know $[A]_0$, $[A]$, and k, and need to find t.

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or $0.200x$. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$
\begin{aligned}
t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\
&= \ln \frac{0.100\ \text{mol L}^{-1}}{0.020\ \text{mol L}^{-1}} \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\
&= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\
&= 1.7 \times 10^{2}\ \text{s}
\end{aligned}
$$

? Exercise 3.4.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. All radioactive decay is first order. How many days will it take for 90% of the iodine−131 in a 0.500 *M* solution of this substance to decay to Xe-131?

Answer

16.7 days

We can use integrated rate laws with experimental data that consist of time and concentration information to determine the order and rate constant of a reaction. The integrated rate law can be rearranged to a standard linear equation format:

$$\ln[A] = (-k)(t) + \ln [A]_0 \tag{3.4.1}$$

$$y = mx + b \tag{3.4.2}$$

A plot of $\ln[A]$ versus t for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $\ln [A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A.

✓ Example 3.4.2: Determination of Reaction Order by Graphing

Show that the data in this Figure can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the rate of decomposition of H_2O_2 from this data.

Solution

The data from this Figure with the addition of values of $\ln[H_2O_2]$ are given in Figure 3.4.1.

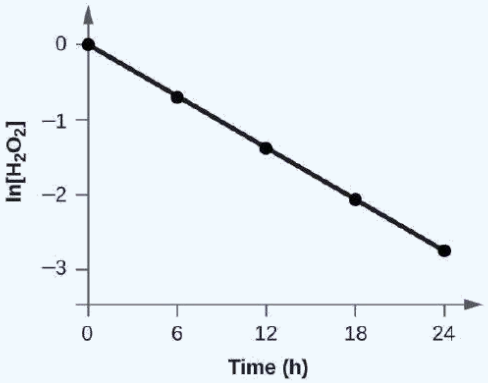


Figure 3.4.1: The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

Solutions to Example 12.4.2

Trial	Time (h)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$
1	0	1.000	0.0
2	6.00	0.500	−0.693
3	12.00	0.250	−1.386
4	18.00	0.125	−2.079
5	24.00	0.0625	−2.772

The plot of $\ln[H_2O_2]$ versus time is linear, thus we have verified that the reaction may be described by a first-order rate law.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[H_2O_2]$ versus time where:

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t}$$

In order to determine the slope of the line, we need two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 6.00 h is −0.693; the value when t = 12.00 h is −1.386:

$$\begin{aligned}\text{slope} &= \frac{-1.386 - (-0.693)}{12.00\ \text{h} - 6.00\ \text{h}} \\ &= \frac{-0.693}{6.00\ \text{h}} \\ &= -1.155 \times 10^{-2}\ \text{h}^{-1} \\ k = -\text{slope} &= -(-1.155 \times 10^{-1}\ \text{h}^{-1}) = 1.155 \times 10^{-1}\ \text{h}^{-1}\end{aligned}$$

? Exercise 3.4.2

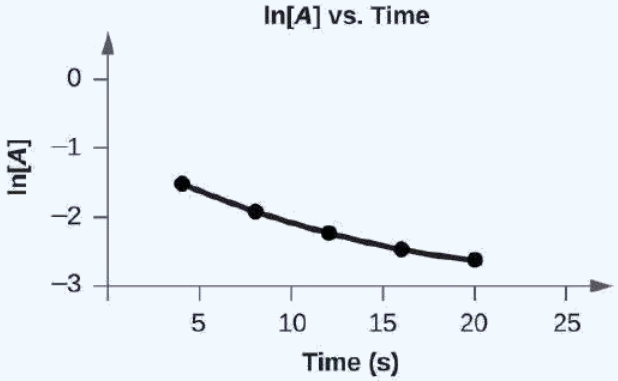
Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Data for the reaction $A \longrightarrow B + C$

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer

The plot of ln[A] vs. t is not a straight line. The equation is not first order:



A graph, labeled above as “l n [A] vs. Time” is shown. The x-axis is labeled, “Time (s)” and the y-axis is labeled, “l n [A].” The x-axis shows markings at 5, 10, 15, 20, and 25 hours. The y-axis shows markings at negative 3, negative 2, negative 1, and 0. A slight curve is drawn connecting five points at coordinates of approximately (4, negative 1.5), (8, negative 2), (12, negative 2.2), (16, negative 2.4), and (20, negative 2.6).

3.4.2: Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions are fairly complicated. We will limit ourselves to the simplest second-order reactions, namely, those with rates that are dependent upon just one reactant’s concentration and described by the differential rate law:

$$\text{Rate} = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{3.4.3}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 3.4.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

$$2\,C_4H_6(g) \longrightarrow C_8H_{12}\,(g)$$

The reaction is second order with a rate constant equal to 5.76×10^{-2} L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration remaining after 10.0 min?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, $k = 5.76 \times 10^{-2}$ L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\frac{1}{[A]} = (5.76 \times 10^{-2}\ \text{L mol}^{-1}\ \text{min}^{-1})(10\ \text{min}) + \frac{1}{0.200\ \text{mol}^{-1}}$$

$$\frac{1}{[A]} = (5.76 \times 10^{-1}\ \text{L mol}^{-1}) + 5.00\ \text{L mol}^{-1}$$

$$\frac{1}{[A]} = 5.58\ \text{L mol}^{-1}$$

$$[A] = 1.79 \times 10^{-1}\ \text{mol L}^{-1}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

Exercise 3.4.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0196 mol/L

The integrated rate law for our second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$
$$y = mx + b$$

A plot of $\frac{1}{[A]}$ versus *t* for a second-order reaction is a straight line with a slope of *k* and an intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 3.4.4: Determination of Reaction Order by Graphing

Test the data given to show whether the dimerization of C_4H_6 is a first- or a second-order reaction.

Solution

Solutions to Example **3.4.4**

Trial	Time (s)	$[C_4H_6]$ (*M*)
1	0	1.00×10^{-2}
2	1600	5.04×10^{-3}
3	3200	3.37×10^{-3}
4	4800	2.53×10^{-3}
5	6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, we plot $\ln[C_4H_6]$ versus *t* and compare it with a plot of $\frac{1}{[C_4H_6]}$ versus *t*. The values needed for these plots follow.

Solutions to Example ✔ **3.4.4**

Time (s)	$\frac{1}{[C_4H_6]}$ (M^{-1})	$\ln[C_4H_6]$
0	100	−4.605
1600	198	−5.289
3200	296	−5.692
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure **3.4.2**. As you can see, the plot of $\ln[C_4H_6]$ versus *t* is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]}$ versus *t* is linear, indicating that the reaction is second order.

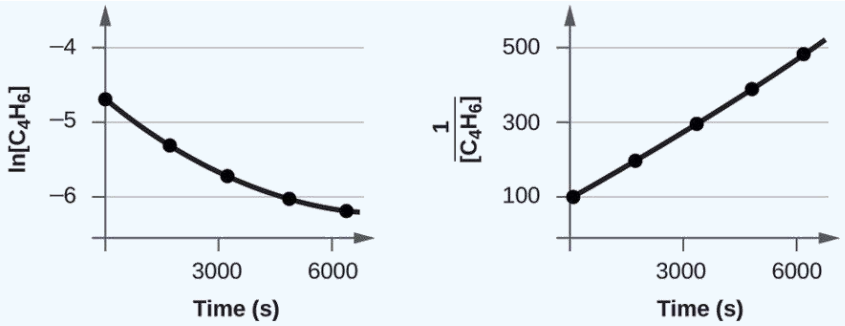


Figure **3.4.2**: These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

Exercise 3.4.4

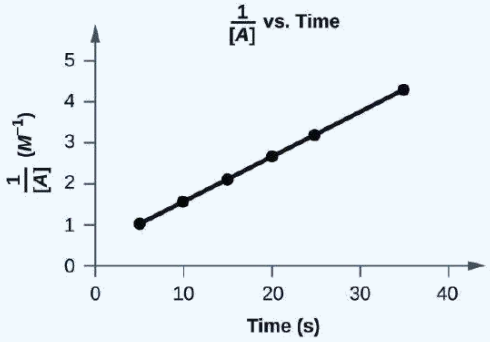
Does the following data fit a second-order rate law?

Data for second-order rate law

Trial	Time (s)	[*A*] (*M*)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer

Yes. The plot of $\frac{1}{[A]}$ vs. t is linear:



A graph, with the title “1 divided by [A] vs. Time” is shown, with the label, “Time (s),” on the x-axis. The label “1 divided by [A]” appears left of the y-axis. The x-axis shows markings beginning at zero and continuing at intervals of 10 up to and including 40. The y-axis on the left shows markings beginning at 0 and increasing by intervals of 1 up to and including 5. A line with an increasing trend is drawn through six points at approximately (4, 1), (10, 1.5), (15, 2.2), (20, 2.8), (26, 3.4), and (36, 4.4).

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3.4.3: Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^0 = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

The integrated rate law for a zero-order reaction also has the form of the equation of a straight line:

$$[A] = -kt + [A]_0$$
$$y = mx + b$$

A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and an intercept of $[A]_0$. Figure **3.4.3** shows a plot of $[NH_3]$ versus t for the decomposition of ammonia on a hot tungsten wire and for the decomposition of ammonia on hot quartz (SiO_2). The decomposition of NH_3 on hot tungsten is zero order; the plot is a straight line. The decomposition of NH_3 on hot quartz is not zero order (it is first order). From the slope of the line for the zero-order decomposition, we can determine the rate constant:

$$\text{slope} = -k = 1.3110^{-6}\ \text{mol/L/s}$$

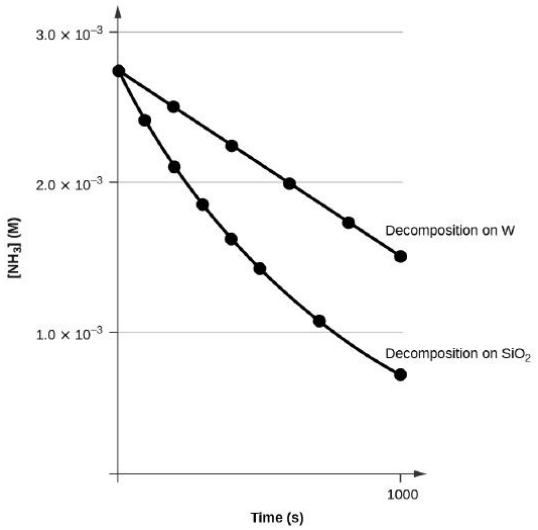


Figure **3.4.3**: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

3.4.4: The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed. Using the decomposition of hydrogen peroxide as an example, we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

3.4.4.1: First-Order Reactions

We can derive an equation for determining the half-life of a first-order reaction from the alternate form of the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]} = kt$$

$$t = \ln \frac{[A]_0}{[A]} \times \frac{1}{k}$$

If we set the time t equal to the half-life, $t_{1/2}$, the corresponding concentration of A at this time is equal to one-half of its initial concentration. Hence, when $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$.

Therefore:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

Thus:

$$t_{1/2} = \frac{0.693}{k}$$

We can see that the half-life of a first-order reaction is inversely proportional to the rate constant k. A fast reaction (shorter half-life) will have a larger k; a slow reaction (longer half-life) will have a smaller k.

Example 3.4.5: Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 3.4.4.



Figure 3.4.4: The decomposition of H_2O_2 ($2H_2O_2 \longrightarrow 2H_2O + O_2$) *at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.*

Solution The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4\ \text{s}} = 3.21 \times 10^{-5}\ \text{s}^{-1}$$

Exercise 3.4.1

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

3.4.4.2: Second-Order Reactions

We can derive the equation for calculating the half-life of a second order as follows:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

If

$$t = t_{1/2}$$

then

$$[A] = \frac{1}{2}[A]_0$$

and we can write:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$2[A]_0 - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

Thus:

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Consequently, we find the use of the half-life concept to be more complex for second-order reactions than for first-order reactions. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

3.4.4.3: Zero-Order Reactions

We can derive an equation for calculating the half-life of a zero order reaction as follows:

$$[A] = -kt + [A]_0$$

When half of the initial amount of reactant has been consumed $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$. Thus:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

and

$$t_{1/2} = \frac{[A]_0}{2k}$$

The half-life of a zero-order reaction increases as the initial concentration increases. Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table **3.4.1**.

Table **3.4.1**: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	M s^{-1}	s^{-1}	M^{-1} s^{-1}
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = +slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Summary

Differential rate laws can be determined by the method of initial rates or other methods. We measure values for the initial rates of a reaction at different concentrations of the reactants. From these measurements, we determine the order of the reaction in each reactant. Integrated rate laws are determined by integration of the corresponding differential rate laws. Rate constants for those rate laws are determined from measurements of concentration at various times during a reaction.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

3.4.5: Key Equations

- integrated rate law for zero-order reactions (Equation ???):

$$[A] = -kt + [A]_0 \text{ with } t_{1/2} = \frac{[A]_0}{2k}$$

- integrated rate law for first-order reactions (Equation 3.4.1):

$$\ln[A] = -kt + \ln[A]_0 \text{ with } t_{1/2} = \frac{0.693}{k}$$

- integrated rate law for second-order reactions (Equation 3.4.3):

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \text{ with } t_{1/2} = \frac{1}{[A]_0 k}$$

Glossary

half-life of a reaction ($t_{1/2}$)

time required for half of a given amount of reactant to be consumed

integrated rate law

equation that relates the concentration of a reactant to elapsed time of reaction

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3.5: First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{3.5.1}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{3.5.2}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 3.5.2 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 3.5.2 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln [A]_0 - kt \tag{3.5.3}$$

Because Equation 3.5.3 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[\text{A}]$ and $b = \ln[\text{A}]_0$, a plot of $\ln[\text{A}]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[\text{A}]_0$. Either the differential rate law (Equation 3.5.1) or the integrated rate law (Equation 3.5.3) can be used to determine whether a particular reaction is first order.

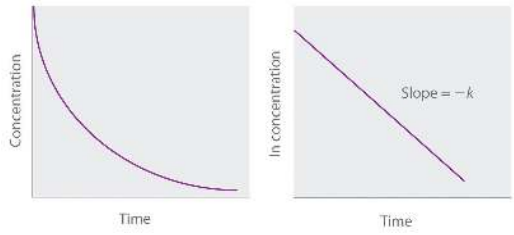


Figure 3.5.1: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. We have already encountered two examples of first-order reactions: the hydrolysis of aspirin and the reaction of *t*-butyl bromide with water to give *t*-butanol. Another reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

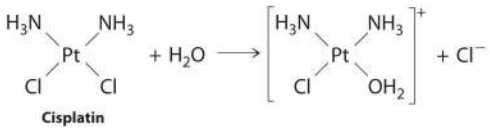


Figure 3.5.2

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 3.5.1 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell

division and tumor growth. Consequently, the kinetics of the reaction in Figure **3.5.1** have been studied extensively to find ways of maximizing the concentration of the active species.

Note

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table **3.5.1**. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin. Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table **3.5.1** shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = k[cisplatin]^1. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table **3.5.1**. For example, substituting the values for Experiment 3 into Equation 3.5.1,

$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$

$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Table **3.5.1**: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 3.5.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$\mathrm{CH_3CH_2Cl(g) \xrightarrow{\Delta} HCl(g) + C_2H_4(g)}$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

Experiment	$[\mathrm{CH_3CH_2Cl}]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.
B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

? Exercise 3.5.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer first order; $k = 2.2 \times 10^{-5}\ \text{s}^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Part (a) in Figure **3.5.3** shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

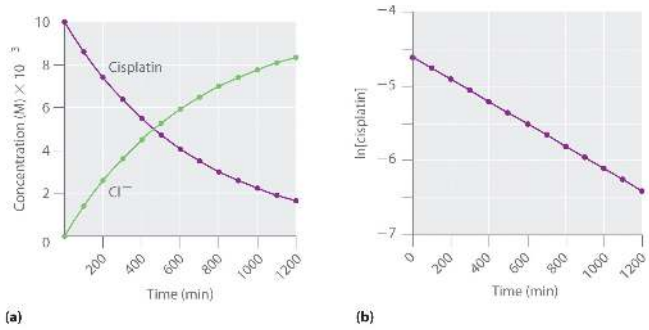


Figure 3.5.3: *The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.*

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 3.5.3. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 3.5.3 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln [\text{cisplatin}]_{1000} - \ln [\text{cisplatin}]_{100}}{1000 \text{ min} - 100 \text{ min}} \tag{3.5.4}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000 \text{ min} - 100 \text{ min}} = \frac{-6.12 - (-4.76)}{900 \text{ min}} = -1.51 \times 10^{-3} \text{ min}^{-1} \tag{3.5.5}$$

$$k = 1.5 \times 10^{-3} \text{ min}^{-1} \tag{3.5.6}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 3.5.3 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.



The First-Order Integrated Rate Law Equation: https://youtu.be/_JskhfxBAMI

Example 3.5.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6}$ s^{-1}) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.

B. Given a concentration [A], solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 3.5.2) is $[A] = [A]_0e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}\ s^{-1}$, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$[CH_3CH_2Cl]_{10\ h} = [CH_3CH_2Cl]_0e^{-kt} \tag{3.5.7}$$

$$= 0.0200\ M(e^{-(1.6\times10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)]}) \tag{3.5.8}$$

$$= 0.0189\ M \tag{3.5.9}$$

We could also have used the logarithmic form of the integrated rate law (Equation 3.5.3):

$$\ln[CH_3CH_2Cl]_{10\ h} = \ln[CH_3CH_2Cl]_0 - kt \tag{3.5.10}$$

$$= \ln 0.0200 - (1.6 \times 10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)] \tag{3.5.11}$$

$$= -3.912 - 0.0576 = -3.970 \tag{3.5.12}$$

$$[CH_3CH_2Cl]_{10\ h} = e^{-3.970}\ M \tag{3.5.13}$$

$$= 0.0189\ M \tag{3.5.14}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 3.5.3 gives the following:

$$\ln[CH_3CH_2Cl]_t = \ln[CH_3CH_2Cl]_0 - kt \tag{3.5.15}$$

$$kt = \ln[CH_3CH_2Cl]_0 - \ln[CH_3CH_2Cl]_t = \ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t} \tag{3.5.16}$$

$$t = \frac{1}{k}\left(\ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6 \times 10^{-6}\ s^{-1}}\left(\ln\frac{0.0200\ M}{0.0050\ M}\right) \tag{3.5.17}$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6}\ s^{-1}} = 8.7 \times 10^5\ s = 240\ h = 2.4 \times 10^2\ h \tag{3.5.18}$$

? Exercise 3.5.2

In the exercise above, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer 0.0252 M; 29 h



Example Using the First-Order Integrated Rate Law Equation:

https://youtu.be/fLY6MtNl9-g

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3.6: Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form 2A → products. A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{2\Delta t} = k[\text{A}]^2 \tag{3.6.1}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt \tag{3.6.2}$$

Because Equation 3.6.2 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[\text{A}]$ and $b = 1/[\text{A}]_0$, a plot of $1/[\text{A}]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[\text{A}]_0$.

> **Note**
>
> Second-order reactions generally have the form 2A → products or A + B → products.

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

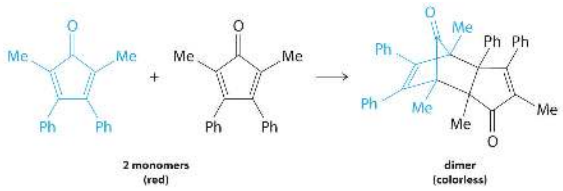


Figure **3.6.1**

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 3.6.1) or the integrated rate law (Equation 3.6.2).

Table **3.6.1**: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table **3.6.1**. From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7 \tag{3.6.3}$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 3.6.1 and the data from any row in Table **3.6.1**, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{3.6.4}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{3.6.5}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{3.6.6}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in part (a) in Figure **3.6.2**. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in part (b) in Figure **3.6.7**. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ \text{M}^{-1}\cdot\text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

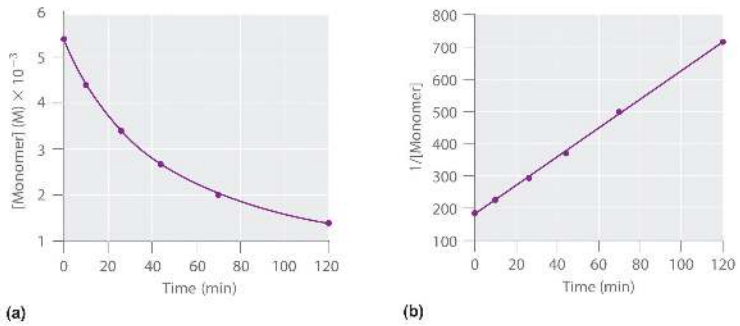


Figure **3.6.2**: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure **3.6.6** as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

Example 3.6.1

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2NO_2(g) \xrightarrow{\Delta} 2NO(g) + O_2(g) \tag{3.6.7}$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\text{rate} = k[NO_2]^2 \tag{3.6.8}$$

$$5.40 \times 10^{-5}\ \text{M/s} = k(0.010\ \text{M})^2 \tag{3.6.9}$$

$$0.54\ \text{M}^{-1} \cdot \text{s}^{-1} = k \tag{3.6.10}$$

Exercise 3.6.1

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer second order in HO_2; $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$

Note

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/reaction concentration versus time is linear, then the reaction is second order.

Example 3.6.2

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 3.6.2) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].
B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 14.4.9,

$$\frac{1}{[NO_2]_{3600}} = \frac{1}{[NO_2]_0} + kt = \frac{1}{0.056\ M} + [(0.54\ M^{-1}\cdot s^{-1})(3600\ s)] \tag{3.6.11}$$

$$= 2.0 \times 10^3\ M^{-1} \tag{3.6.12}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056$ M. To do this, we solve Equation 3.6.2 for t, using the concentrations given.

$$t = \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} = \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1}\cdot s^{-1}} = 3.0 \times 10^2\ s = 5.0\ min$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 3.6.2

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the

concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 3.6.2) and the rate constant calculated in the exercise in Example 3.6.3.

Answer 2.0×10^{-13} M; 6.4×10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = k[\text{A}][\text{B}] \tag{3.6.13}$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.



Second-Order Integrated Rate Law Equation: https://youtu.be/hMSgk2Rm2xA

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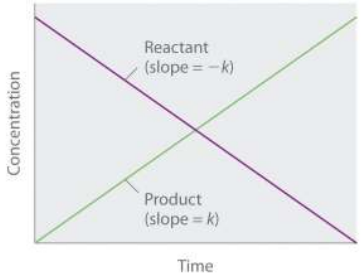
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3.7: Zero-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is rate = k. We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{3.7.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.



The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{3.7.2}$$

where $[\text{A}]_0$ is the initial concentration of reactant A. Equation 3.7.2 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = [\text{A}]$, $mx = -kt$, and $b = [\text{A}]_0$.) In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2\text{N}_2\text{O}(\text{g}) \xrightarrow{\text{Pt}} 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \tag{3.7.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\text{N}_2\text{O}]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[\text{N}_2]}{\Delta t}\right) = \frac{\Delta[\text{O}_2]}{\Delta t} = k[\text{N}_2\text{O}]^0 = k \tag{3.7.4}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure **3.7.1**, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

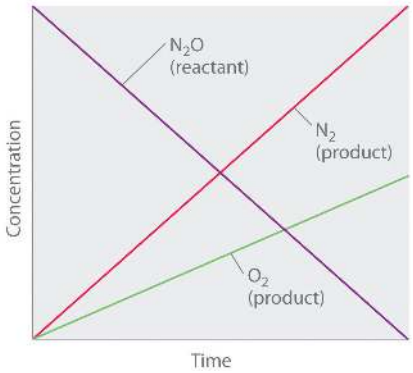


Figure **3.7.1***: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.*

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

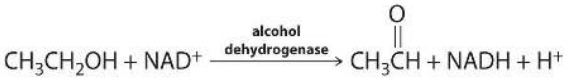


Figure **3.7.2**

where NAD^+ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (part (a) in Figure **3.7.3**). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure **3.7.3**).

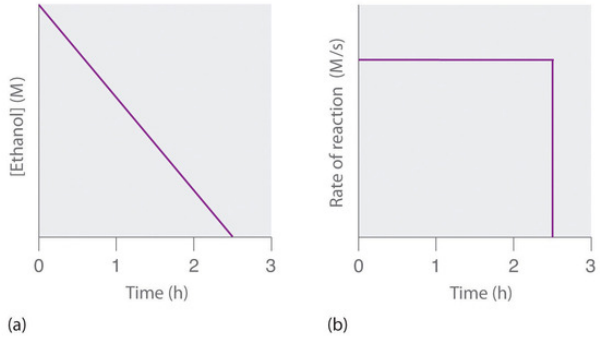


Figure **3.7.3**: The Catalyzed Oxidation of Ethanol *(a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.*

These examples illustrate two important points:

1. *In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.*
2. *A linear change in concentration with time is a clear indication of a zeroth-order reaction.*



Zero-Order Reactions: https://youtu.be/64i7uYsVsSs

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3.8: Pseudo-1st-order reactions

Under certain conditions, the 2nd order kinetics can be approximated as first-order kinetics. These **pseudo-1st-order reactions** greatly simplify quantifying the reaction dynamics.

Introduction

A 2nd-order reaction can be challenging to follow mostly because the two reactants involved must be measured simultaneously. There can be additional complications because certain amounts of each reactant are required to determine the reaction rate, for example, which can make the cost of one's experiment high if one or both of the needed reactants are expensive. To avoid more complicated, expensive experiments and calculations, we can use the pseudo-1st-order reaction, which involves treating a 2nd order reaction like a 1st order reaction.

In second-order reactions with two reactant species,

$$\mathbf{A + B \longrightarrow products}$$

the rate of disappearance of A is

$$\frac{d[A]}{dt} = -k[A][B]$$

as discussed previously (Case 2a), the integrated rate equation under the condition that [A] and [B] are not equal is

$$\frac{1}{[B]_o - [A]_o} \ln \frac{[B][A]_o}{[A][B]_o} = kt \tag{3.8.1}$$

However, when $[B]_0 \gg [A]_0$, then $[B]_0 \approx [B]$ and Equation 3.8.1 becomes

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[B][A]_0}{[B]_0[A]} \approx \frac{1}{[B]} \ln \frac{[A]_0}{[A]} = kt$$

or

$$[A] = [A]_0 e^{-[B]kt}$$

This functional form of the decay kinetics is similar ot the first order kinetics and the system is said to operate under pseudo-first order kinetics. To reach a pseudo-1st-order reaction, we can manipulate the initial concentrations of the reactants. One of the reactants, **B**, for example, would have a significantly higher concentration, while the other reactant, A, would have a significantly lower concentration. We can then assume that the concentration of reactant B effectively remains constant during the reaction because its consumption is so small that the change in concentration becomes negligible. Because of this assumption, we can multiply the reaction rate, k, with the reactant with assumed constant concentration, B, to create a new rate constant ($k' = k[B]$) that will be used in the new rate equation,

$$\mathbf{Rate} = k'[A]$$

as the new rate constant so we can treat the 2nd order reaction as a 1st order reaction.

Overloading

One can also do the same by overloading the initial concentration of A so that it effectively remains constant during the course of the reaction For example, if one were to dump a liter of 5 M $\mathbf{HCl}$ into a 55 M ocean, the concentration of the mixture would be closer or equal to that of the ocean because there is so much water physically compared to the $\mathbf{HCl}$. Even if the amount of water was one liter this would still be the case because 55 M is relatively large compared to 5 M.

If we have an instance where there are more than two reactants involved in a reaction, all we would have to do to make the reaction pseudo-1st-order is to make the concentrations of all but one of the reactants very large. If there were three reactants, for example, we would make two of the three reactants be in excess (whether in amount or in concentration) and then monitor the dependency of the third reactant.

We can write the pseudost-order reaction equation as:

$$[A] = [A]_0 e^{-[B]_0 kt} \tag{3.8.2}$$

or

$$[A] = [A]_0 e^{-k't}$$

where

- $[A]_o$ is the initial concentration of A,
- $[B]_o$ is the initial concentration of B,
- k' is the pseudo-1st-order reaction rate constant,
- k is the 2nd order reaction rate constant, and
- $[A]$ is the concentration of A at time t.

By using natural log to both sides of the pseudo-1st-order equation we get:

$$\ln\left(\frac{A}{A_0}\right) = -k[B]_0 t$$

or

$$\ln\left(\frac{A}{A_0}\right) = -k't$$

Example 3.8.1

If a 2nd order reaction has the rate equation $\text{Rate} = k[A][B]$, and the rate constant, k, is $3.67\,M^{-1}s^{-1}$, $[A]$ is $4.5\,M$ and $[B]$ is $99\,M$, what is the rate constant of its pseudo-1st-order reaction?

Solution

Because $[B]$ is in excess we multiply $99\,M$ with $3.67\,M^{-1}s^{-1}$

$$(99\,M)(3.67\,M^{-1}s^{-1}) = 363.33\,s^{-1}$$

Example 3.8.2

If [A] = 55 M at 39 s, $[A]_o$ = 99 M, and $[B]_o$ = 1000 M, what is the 2nd order reaction rate constant?

Solution

Use the Equation 3.8.2

$$(55\text{ M}) = (99\text{ M})e^{-k'(1000\text{M})(39\text{s})}$$

$$k' = 1.507 \times 10^{-5}\ \text{M}^{-1}\text{s}^{-1}$$

Example 3.8.3

What is the concentration of A at time 45 s if $[A]_o$ = 1M, $[B]_o$ = 45 M, and 2nd order rate constant is 0.6 $M^{-1}s^{-1}$?

Solution

Use the Equation 3.8.2

$[A] = (1)e^{-(0.6\ \text{M-1s-1})(45)}$

$[A] = 1.88 \times 10^{-12}$ M

Example 3.8.4

What is the rate of a reaction if $[A]_o$ = 560 M, $[B]_o$ = 0.2M, and 2nd order rate constant is 0.1 $M^{-1}s^{-1}$?

Solution

Use the equation R = k'[A][B]

R = $(0.1M^{-1}s^{-1})(560M)(0.2M)$

Rate = $11.2Ms^{-1}$

Half-Life in a Pseudo-1st Order reaction

Half-life refers to the time required to decrease the concentration of a reactant by half, so we must solve for t. Here, $[B]$ will be the reactant in excess, and its concentration will stay constant. $[A]_o$ is the initial concentration of A; thus the half-life concentration of A is $0.5[A]_o$.

The pseudo-1st-order reaction equation can be written as:

$$[A] = [A]_o e^{-[B]kt} \quad or \quad \frac{[A]}{[A]_o} = e^{-k't}$$

By taking natural logs on both sides of the pseudo-1st-order equation, we get:

$$\ln\left(\frac{[A]}{[A]_o}\right) = k't$$

Because the concentration of A for a half-life $t_{1/2}$ is $1/2[A]_o$:

$$\ln\left(\frac{1/2[A]_o}{[A]_o}\right) = \ln\left(\frac{1}{2}\right) = -k't_{1/2}$$

Recalling that $k' = k[B]$, $[B] \approx [B]_0$ and that $-\ln(1/2) = \ln 2$:

$$\ln(2) = k[B]_0 t_{1/2}$$

or

$$t_{1/2} = \frac{\ln 2}{k[B]_0}$$

Example 3.8.5

What is the half-life of a reaction with $[A]_o$ = 109 M, $[B]_o$ = 1 M, k' = 45 $M^{-1}s^{-1}$?

Solution

Because [A] is in excess we can multiply the k' with $[A]_o$ to find k

$$(109M)(45M^{-1}s^{-1}) = 4905s^{-1}$$

$$t_{1/2} = (\ln 0.5 / -k)$$

$$t_{1/2} = 1.41 \text{ X } 10^{-4}s$$

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3.9: Reaction Mechanisms

Learning Objectives

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The reaction mechanism (or reaction path) is the process, or pathway, by which a reaction occurs. A chemical reaction often occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$\begin{aligned} &O_3(g) \longrightarrow O_2(g) + O \\ &O + O_3(g) \longrightarrow 2\,O_2(g) \end{aligned} \tag{3.9.1}$$

We call each step in a reaction mechanism an elementary reaction. Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{3.9.2}$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

3.9.0.0.1: Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the rearrangement of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{products} \tag{3.9.3}$$

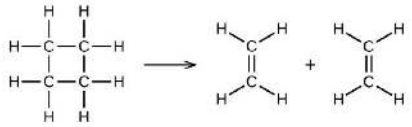
The rate equation for a unimolecular reaction is:

$$\text{rate} = k[A] \tag{3.9.4}$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O \tag{3.9.5}$$

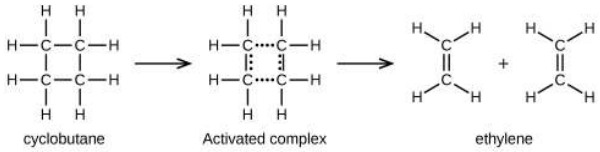
illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, occurs via a unimolecular, single-step mechanism:



In this figure, structural formulas are used to illustrate a chemical reaction. On the left, a structural formula for cyclobutane is shown. This structure is composed of 4 C atoms connected with single bonds in a square shape. Each C atom is bonded to two other C atoms in the structure, leaving two bonds for H atoms pointing outward above, below, left, and right. An arrow points right to two identical ethane molecules with a plus symbol between them. Each of these molecules contains two C atoms connected with a double bond oriented vertically between them. The C atom at the top of these molecules has H atoms bonded above to the right and left. Similarly, the lower C atom has two H atoms bonded below to the right and left.

For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of C_4H_8, for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In this figure, structural formulas are used to illustrate a chemical reaction, including an intermediate step. On the left, a structural formula for cyclobutane is shown. This structure is composed of 4 C atoms connected with single bonds in a square shape. Each C atom is bonded to two other C atoms in the structure, leaving two bonds for H atoms pointing outward above, below, left, and right. This structure is labeled, “Cyclohexane.” An arrow points right to a similar structure which has the upper and lower bonds replaced by rows of 4 dots. Similarly, columns of 3 dots appear just inside the line segments indicating the vertically oriented single bonds in the structure. The label “Activated complex” appears beneath this structure. A second arrow points right to two identical ethane molecules with a plus symbol between them. Each of these molecules contains two C atoms connected with a double bond oriented vertically between them. The C atom at the top of these molecules has H atoms bonded above to the right and left. Similarly, the lower C atom has two H atoms bonded below to the right and left. Below these two molecules appears the label “Ethylene.”

In a sample of C_4H_8, a few of the rapidly moving C_4H_8 molecules collide with other rapidly moving molecules and pick up additional energy. When the C_4H_8 molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a C_4H_8 molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

The rate of decomposition of C_4H_8 is directly proportional to its concentration. Doubling the concentration of C_4H_8 in a sample gives twice as many molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much C_4H_8 per liter, and the reaction rate is twice as fast:

$$\text{rate} = -\frac{\Delta[C_4H_8]}{\Delta t} = k[C_4H_8] \tag{3.9.6}$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

3.9.1: Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a bimolecular reaction. There are two types of bimolecular elementary reactions:

$$A + B \longrightarrow \text{products} \tag{3.9.7}$$

and

$$2A \longrightarrow \text{products} \tag{3.9.8}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B*:

$$\text{rate} = k[A][B] \tag{3.9.9}$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate} = k[A][A] = k[A]^2 \tag{3.9.10}$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \tag{3.9.11}$$

(see Figure **3.9.1**)

Figure **3.9.1**: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

This figure provides an illustration of a reaction between two H I molecules using space filling models. H atoms are shown as white spheres, and I atoms are shown as purple spheres. On the left, two H I molecules are shownwith a small white sphere bonded to a much larger purple sphere. The label, “Two H I molecules,” appears below. An arrow points right to a similar structure in which the two molecules appear pushed together, so that the purple spheres of the two molecules are touching. Below appears the label, “Transition state.” Following another arrow, two white spheres are shown vertically oriented and bonded together with the label, “H subscript 2” above. The H subscript 2 molecule is followed by a plus sign and two purple spheres bonded together with the label, “I subscript 2” above. Below these structures is the label, “Hydrogen iodide molecules decompose to produce hydrogen H subscript 2 and iodine I subscript 2.”

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

$$O(g) + O_3(g) \longrightarrow 2\,O_2(g) \tag{3.9.12}$$

3.9.1.0.1: 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:

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \tag{3.9.13}$$
$$\text{rate} = k[NO]^2[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2\,NO + Cl_2 \longrightarrow 2\,NOCl \tag{3.9.14}$$
$$\text{rate} = k[NO]^2[Cl_2]$$

3.9.1.0.1: Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure **3.9.2**.



Figure **3.9.2**: 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)

A photo is shown of cattle passing through a narrow chute into a holding pen. A person directs them through the gate with a long white and red pole.

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, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

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 is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:

$$\begin{aligned}&\mathrm{NO_2}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{NO_3}(g) + \mathrm{NO}(g)\ \text{(slow)}\\&\mathrm{NO_3}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{CO_2}(g)\ \text{(fast)}\end{aligned}$$

The rate-determining step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N_2O_2, with k_1 used to represent the rate constant of the forward reaction and k_{-1} used to represent the rate constant of the reverse reaction:

$$\mathrm{NO} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2}$$

$$\mathrm{rate_{forward}} = \mathrm{rate_{reverse}}$$

$$k_1[\mathrm{NO}]^2 = k_{-1}[\mathrm{N_2O_2}]$$

If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

$$\left(\frac{k_1[\mathrm{NO}]^2}{k_{-1}}\right) = [\mathrm{N_2O_2}]$$

However, once again, intermediates cannot be listed as part of the overall rate law expression, though they can be included in an individual elementary reaction of a mechanism. Example **3.9.1** will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 3.9.1: Deriving the Overall Rate Law Expression for a Multistep Reaction

Mechanism Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

1. $\mathrm{2\,NO_2Cl}(g) \rightleftharpoons \mathrm{ClO_2}(g) + \mathrm{N_2O}(g) + \mathrm{ClO}(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)
2. $\mathrm{N_2O}(g) + \mathrm{ClO_2}(g) \rightleftharpoons \mathrm{NO_2}(g) + \mathrm{NOCl}(g)$ (fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)
3. $\mathrm{NOCl} + \mathrm{ClO} \longrightarrow \mathrm{NO_2} + \mathrm{Cl_2}$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:

$$\mathrm{2\,NO_2Cl}(g) \longrightarrow \mathrm{2\,NO_2}(g) + \mathrm{Cl_2}(g)$$

Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

$$\begin{aligned}k_1[\mathrm{NO_2Cl}]_2 &= k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}][\mathrm{ClO}]\\k_2[\mathrm{N_2O}][\mathrm{ClO_2}] &= k_{-2}[\mathrm{NO_2}][\mathrm{NOCl}]\\\mathrm{Rate} &= k_3[\mathrm{NOCl}][\mathrm{ClO}]\end{aligned}$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate law expression could be written as Rate = k_3 [NOCl][ClO]. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent [NOCl] and [ClO] such that no intermediates remain in the overall rate law expression.

- Using elementary reaction 1, $[\mathrm{ClO}] = \dfrac{k_1[\mathrm{NO_2Cl}]^2}{k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}]}$.
- Using elementary reaction 2, $[\mathrm{NOCl}] = \dfrac{k_2[\mathrm{N_2O}][\mathrm{ClO_2}]}{k_{-2}[\mathrm{NO_2}]}$.

Now substitute these algebraic expressions into the overall rate law expression and simplify:

$$\begin{aligned}\mathrm{rate} &= k_3\left(\frac{k_2[\mathrm{N_2O}][\mathrm{ClO_2}]}{k_{-2}[\mathrm{NO_2}]}\right)\left(\frac{k_1[\mathrm{NO_2Cl}]^2}{k_{-1}[\mathrm{ClO_2}][\mathrm{N_2O}]}\right)\\\mathrm{rate} &= \frac{k_3k_2k_1[\mathrm{NO_2Cl}]^2}{k_{-2}k_{-1}[\mathrm{NO_2}]}\end{aligned}$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

Exercise 3.9.1

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:

$$\begin{aligned}&\mathrm{Cl} + \mathrm{O_3}(g) \longrightarrow \mathrm{ClO}(g) + \mathrm{O_2}(g) \quad (\text{rate constant } k_1)\\&\mathrm{ClO}(g) + \mathrm{O} \longrightarrow \mathrm{Cl}(g) + \mathrm{O_2}(g) \quad (\text{rate constant } k_2)\end{aligned}$$

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Answer

- overall reaction: $\mathrm{O_3}(g) + \mathrm{O} \longrightarrow \mathrm{2\,O_2}(g)$
- $\mathrm{rate}_1 = k_1[\mathrm{O_3}][\mathrm{Cl}]$; $\mathrm{rate}_2 = k_2[\mathrm{ClO}][\mathrm{O}]$
- intermediate: ClO(g)
- overall rate = $k_2k_1[\mathrm{O_3}][\mathrm{Cl}][\mathrm{O}]$

Summary

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

3.9.1.1: Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

3.9.1.2: Glossary

bimolecular reaction
elementary reaction involving the collision and combination of two reactant species

elementary reaction
reaction that takes place precisely as depicted in its chemical equation

intermediate
molecule or ion produced in one step of a reaction mechanism and consumed in another

molecularity
number of reactant species (atoms, molecules or ions) involved in an elementary reaction

rate-determining step
(also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction mechanism
stepwise sequence of elementary reactions by which a chemical change takes place

termolecular reaction
elementary reaction involving the simultaneous collision and combination of three reactant species

unimolecular reaction
elementary reaction involving the rearrangement of a single reactant species to produce one or more molecules of product

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3.10: The Collision Theory

Collision theory explains why different reactions occur at different rates, and suggests ways to change the rate of a reaction. Collision theory states that for a chemical reaction to occur, the reacting particles must collide with one another. The rate of the reaction depends on the frequency of collisions. The theory also tells us that reacting particles often collide ***without*** reacting. For collisions to be successful, reacting particles must (1) collide with (2) sufficient energy, and (3) with the proper orientation.

Molecules must collide before they can react

This rule is fundamental to any analysis of an ordinary reaction mechanism. It explains why termolecular processes are so uncommon. The kinetic theory of gases states that for every 1000 binary collisions, there will be only one event in which three molecules simultaneously come together. Four-way collisions are so improbable that this process has never been demonstrated in an elementary reaction.



Consider a simple bimolecular step:

$$A + B \rightarrow Products$$

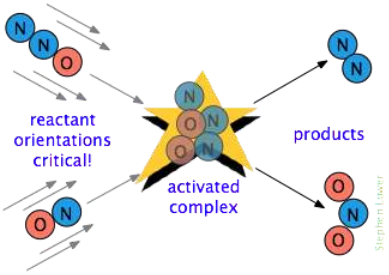
If the two molecules A and B are to react, they must approach closely enough to disrupt some of their existing bonds and to permit the creation of any new ones that are needed in the products. Such an encounter is called a *collision*.

The frequency of collisions between A and B in a gas is proportional to the concentration of each; if [A] is doubled, the frequency of A-B collisions will double, and doubling [B] will have the same effect. If all collisions lead to products, then the rate of a bimolecular process is first-order in A and in B, or second-order overall:

$$rate = k[A][B]$$

Not all Collisions are Equal

For a gas at room temperature and normal atmospheric pressure, there are about 10^{33} collisions in each cubic centimeter of space every second. If every collision between two reactant molecules yielded products, all reactions would be complete in a fraction of a second. For example, when two billiard balls collide, they simply bounce off of each other. This is the most likely outcome if the reaction between A and B requires a significant disruption or rearrangement of the bonds between their atoms. In order to effectively initiate a reaction, collisions must be sufficiently *energetic* (or have sufficient kinetic energy) to bring about this bond disruption. This is further discussed below.



There is often one additional requirement. In many reactions, especially those involving more complex molecules, the reacting species must be oriented in a manner that is appropriate for the particular process. For example, in the gas-phase reaction of dinitrogen oxide with nitric oxide, the oxygen end of N_2O must hit the nitrogen end of NO; altering the orientation of either

molecule prevents the reaction. Owing to the extensive randomization of molecular motions in a gas or liquid, there are always enough correctly-oriented molecules for some of the molecules to react. However, the more critical this orientational requirement is, the fewer collisions will be effective.

Energetic collisions between molecules cause interatomic bonds to stretch and bend, temporarily weakening them so that they become more susceptible to cleavage. Distortion of the bonds can expose their associated electron clouds to interactions with other reactants that might lead to the formation of new bonds.

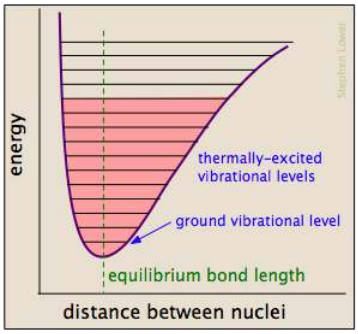


Figure 2: Anatomy of a collision

Chemical bonds have some of the properties of mechanical springs: their potential energies depend on the extent to which they are stretched or compressed. Each atom-to-atom bond can be described by a potential energy diagram that shows how its energy changes with its length. When the bond absorbs energy (either from heating or through a collision), it is elevated to a higher quantized vibrational state (indicated by the horizontal lines) that weakens the bond as its length oscillates between the extended limits corresponding to the curve.

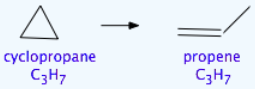
A particular collision will typically excite a number of bonds in this way. Within about 10^{-13} seconds, this excitation is distributed among the other bonds in the molecule in complex and unpredictable ways that can concentrate the added energy at a particularly vulnerable point. The affected bond can stretch and bend farther, making it more susceptible to cleavage. Even if the bond does not break by pure stretching, it can become distorted or twisted so as to expose nearby electron clouds to interactions with other reactants that might encourage a reaction.

Unimolecular processes also begin with a collision

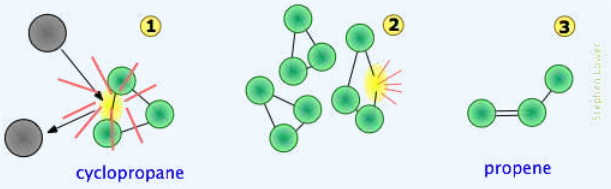
Until about 1921, chemists did not understand the role of collisions in unimolecular processes. It turns out that the mechanisms of such reactions are actually quite complicated, and that at very low pressures they do follow second-order kinetics. Such reactions are more properly described as *pseudounimolecular*. The cyclopropane isomerization described in Example 1 is typical of many decomposition reactions found to follow first-order kinetics, implying that the process is unimolecular.

Example 1: Isomerization of Cyclopropane

Consider, for example, the isomerization of cyclopropane to propene, which takes place at fairly high temperatures in the gas phase.



The collision-to-product sequence can be conceptualized in the following [grossly oversimplified] way:



Note that

- For simplicity, the hydrogen atoms are not shown here. This is reasonable because C–C bonds are weaker then C–H bonds, which are less likely to be affected.
- The collision at (1) is most likely with another cyclopropane molecule, but because no part of the colliding molecule gets incorporated into the product, it can in principle be a noble gas or some other non-reacting species;
- Although the C–C bonds in cyclopropane are all identical, the instantaneous localization of the collisional energy can distort the molecule in various ways ((2)), leading to a configuration sufficiently unstable to initiate the rearrangement to the product.

Note: In the Classroom

Here are some simple little "experiments" to help illustrate this concepts. These are "thought experiments," to be reasoned out rather than actually performed.

In an empty classroom, blindfold a group of 10 or so students and instruct them to walk slowly around the room. Occasionally, a pair of students will bump into one another. If they are moving slowly enough, nothing much will happen (that is, no pain upon contact). But if these blindfolded students begin running around the room (more speed means more energy), then a collision is likely to be successful (painfully so). If some students move about quickly, while others stroll about at a more leisurely pace, successful reactions will still occur, but not as often as if all students are running.

Next, have the students move at a brisk pace, but without running. This time, however, consider that collisions that occur shoulder-to-shoulder are not successful—shoulders act as sufficient bumpers and collisions are not painful. But if one student steps on another's toes, then a successful collision occurs. Let the movement begin. Of the frequent collisions that result, only a few will involve one student stepping on another's toes. This experiment illustrates that collisions must occur with the proper orientation. Again, collisions between students will occur, but only some will be successful.

Factors that increase the rate of a reaction must influence at least one of the following:

- how often collisions occur. More frequent collisions will mean a faster rate.
- more effective collisions in terms of collisions occurring with sufficient energy
- more effective collisions in terms of collisions occurring with the proper orientation.

Two more topics must be examined before these can be discussed in depth: reaction mechanisms and the concept of threshold energy.

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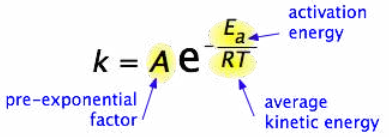
3.11: Arrhenius Equation

It is common knowledge that chemical reactions occur more rapidly at higher temperatures. Milk turns sour much more rapidly if stored at room temperature rather than in a refrigerator; butter goes rancid more quickly in the summer than in the winter; and eggs hard-boil more quickly at sea level than in the mountains. For the same reason, cold-blooded animals such as reptiles and insects tend to be more lethargic on cold days.

The reason for this is not hard to understand. Thermal energy relates direction to motion at the molecular level. As the temperature rises, molecules move faster and collide more vigorously, greatly increasing the likelihood of bond cleavages and rearrangements. Whether it is through the collision theory, transition state theory, or just common sense, chemical reactions are typically expected to proceed faster at higher temperatures and slower at lower temperatures.



By 1890 it was common knowledge that higher temperatures speed up reactions, often doubling the rate for a 10-degree rise, but the reasons for this were not clear. Finally, in 1899, the Swedish chemist Svante Arrhenius (1859-1927) combined the concepts of activation energy and the Boltzmann distribution law into one of the most important relationships in physical chemistry:



Take a moment to focus on the meaning of this equation, neglecting the *A* factor for the time being. First, note that this is another form of the exponential decay law discussed in the previous section of this series. What is "decaying" here is not the concentration of a reactant as a function of time, but the magnitude of the rate constant as a function of the exponent $-E_a/RT$. And what is the significance of this quantity? Recalling that *RT* is the *average kinetic energy*, it becomes apparent that the exponent is just the ratio of the activation energy E_a to the average kinetic energy. The larger this ratio, the smaller the rate (hence the negative sign). This means that high temperature and low activation energy favor larger rate constants, and thus speed up the reaction. Because these terms occur in an exponent, their effects on the rate are quite substantial.

The two plots below show the effects of the activation energy (denoted here by $E^{\ddagger}$) on the rate constant. Even a modest activation energy of 50 kJ/mol reduces the rate by a factor of 10^8.

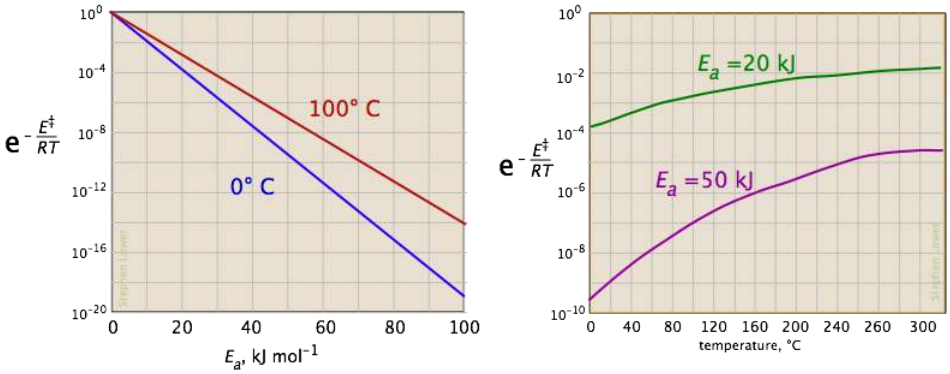


Figure 3.11.1: Arrhenius plots. The logarithmic scale in the right-hand plot leads to nice straight lines.

Looking at the role of temperature, a similar effect is observed. (If the *x*-axis were in "kilodegrees" the slopes would be more comparable in magnitude with those of the kilojoule plot at the above right.)

Determining the Activation Energy

The Arrhenius equation,

$$k = Ae^{-E_a/RT} \tag{3.11.1}$$

can be written in a non-exponential form that is often more convenient to use and to interpret graphically. Taking the logarithms of both sides and separating the exponential and pre-exponential terms yields

$$\ln k = \ln\left(Ae^{-E_a/RT}\right) \tag{3.11.2}$$

$$= \ln A + \ln\left(e^{-E_a/RT}\right) \tag{3.11.3}$$

$$= \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \tag{3.11.4}$$

Equation 3.11.4 is in the form of $y = mx + b$ - the equation of a straight line.

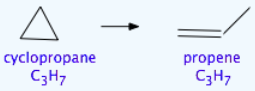
$$\ln k = \ln A - \frac{E_a}{RT}$$

where temperature is the independent variable and the rate constant is the dependent variable. So if one were given a data set of various values of k, the rate constant of a certain chemical reaction at varying temperature T, one could graph $\ln(k)$ versus $1/T$. From the graph, one can then determine the slope of the line and realize that this value is equal to $-E_a/R$. One can then solve for the activation energy by multiplying through by -R, where R is the gas constant.

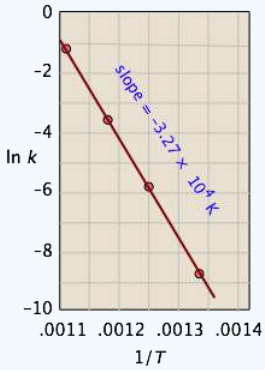
This affords a simple way of determining the activation energy from values of *k* observed at different temperatures, by plotting $\ln k$ as a function of $1/T$.

Example 3.11.1: Isomerization of Cyclopropane

For the isomerization of cyclopropane to propene,



the following data were obtained (calculated values shaded in pink):



T, °C	477	523	577	623
$1/T$, $K^{-1} \times 10^3$	1.33	1.25	1.18	1.11
k, s^{-1}	0.00018	0.0027	0.030	0.26
ln k	–8.62	–5.92	–3.51	–1.35

From the calculated slope, we have

$$-\left(\frac{E_a}{R}\right) = -3.27 \times 10^4 K$$
$$E_a = -(8.314\, J\, mol^{-1} K^{-1})(-3.27 \times 10^4\, K)$$
$$= 273\, kJ\, mol^{-1}$$

Comment: This activation energy is high, which is not surprising because a carbon-carbon bond must be broken in order to open the cyclopropane ring. (C–C bond energies are typically around 350 kJ/mol.) This is why the reaction must be carried out at high temperature.

Calculating E_a without a plot

Because the ln k-vs.-$1/T$ plot yields a straight line, it is often convenient to estimate the activation energy from experiments at only two temperatures. To see how this is done, consider that

$$\ln k_2 - \ln k_1 = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right)$$
$$= \boxed{\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

The ln-A term is eliminated by subtracting the expressions for the two ln-k terms.) Solving the expression on the right for the activation energy yields

$$E_a = \frac{R \ln \dfrac{k_2}{k_1}}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

Example 3.11.2

A widely used rule-of-thumb for the temperature dependence of a reaction rate is that a **ten degree** rise in the temperature approximately doubles the rate. This is not generally true, especially when a strong covalent bond must be broken. For a reaction that does show this behavior, what would the activation energy be?

Solution

Center the ten degree interval at 300 K. Substituting into the above expression yields

$$E_a = \frac{(8.314)(\ln 2/1)}{\frac{1}{295} - \frac{1}{305}}$$
$$= \frac{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(0.693)}{0.00339\,\text{K}^{-1} - 0.00328\,\text{K}^{-1}}$$
$$= \frac{5.76\,J\,mol^{-1}K^{-1}}{(0.00011\,K^{-1}}$$
$$= 52,400\,J\,mol^{-1} = 52.4\,kJ\,mol^{-1}$$

Example 3.11.3

It takes about 3.0 minutes to cook a hard-boiled egg in Los Angeles, but at the higher altitude of Denver, where water boils at 92°C, the cooking time is 4.5 minutes. Use this information to estimate the activation energy for the coagulation of egg albumin protein.

Solution

The ratio of the rate constants at the elevations of Los Angeles and Denver is 4.5/3.0 = 1.5, and the respective temperatures are **373 K** and **365 K**. With the subscripts 2 and 1 referring to Los Angeles and Denver respectively:

$$E_a = \frac{(8.314)(\ln 1.5)}{\frac{1}{365\ \text{K}} - \frac{1}{373\ \text{K}}}$$
$$= \frac{(8.314)(0.405)}{0.00274\ \text{K}^{-1} - 0.00268\ \text{K}^{-1}}$$
$$= \frac{(3.37\ \text{J mol}^{-1}\text{K}^{-1})}{5.87 \times 10^{-5}\ \text{K}^{-1}}$$
$$= 57,400\ \text{J mol}^{-1}$$
$$= 57.4\ \text{kJ mol}^{-1}$$

Comment: This low value seems reasonable because thermal denaturation of proteins primarily involves the disruption of relatively weak hydrogen bonds; no covalent bonds are broken (although disulfide bonds can interfere with this interpretation).

The Pre-exponential Factor

Up to this point, the pre-exponential term, A in the Arrhenius equation (Equation 3.11.1), has been ignored because it is not directly involved in relating temperature and activation energy, which is the main practical use of the equation.

$$k = Ae^{-E_a/RT}$$

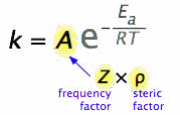
However, because A multiplies the exponential term, its value clearly contributes to the value of the rate constant and thus of the rate. Recall that the exponential part of the Arrhenius equation expresses the fraction of reactant molecules that possess enough kinetic energy to react, as governed by the Maxwell-Boltzmann law. This fraction can run from zero to nearly unity, depending on the magnitudes of E_a and of the temperature.

If this fraction were 0, the Arrhenius law would reduce to

$$k = A$$

In other words, A is the fraction of molecules that would react if either the activation energy were zero, or if the kinetic energy of all molecules exceeded E_a — admittedly, an uncommon scenario (although barrierless reactions have been characterized).

What would limit the rate constant if there were no activation energy requirements? The most obvious factor would be the rate at which reactant molecules come into contact. This can be calculated from kinetic molecular theory and is known as the **frequency-** or **collision factor**, Z.



In some reactions, the relative orientation of the molecules at the point of collision is important, so a geometrical or **steric factor** (commonly denoted by ρ) can be defined. In general, we can express A as the product of these two factors:

$$A = Z\rho$$

Values of ρ are generally very difficult to assess; they are sometime estimated by comparing the observed rate constant with the one in which A is assumed to be the same as Z.

Implications

The exponential term in the Arrhenius equation implies that the rate constant of a reaction increases exponentially when the activation energy decreases. Because the rate of a reaction is directly proportional to the rate constant of a reaction, the rate increases exponentially as well. Because a reaction with a small activation energy does not require much energy to reach the transition state, it should proceed faster than a reaction with a larger activation energy.

In addition, the Arrhenius equation implies that the rate of an uncatalyzed reaction is more affected by temperature than the rate of a catalyzed reaction. This is because the activation energy of an uncatalyzed reaction is greater than the activation energy of the corresponding catalyzed reaction. Since the exponential term includes the activation energy as the numerator and the temperature as the denominator, a smaller activation energy will have less of an impact on the rate constant compared to a larger activation energy. Hence, the rate of an uncatalyzed reaction is more affected by temperature changes than a catalyzed reaction.

The Math in Eliminating the Constant A

To eliminate the constant A, there must be two known temperatures and/or rate constants. With this knowledge, the following equations can be written:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \tag{3.11.5}$$

at T_1 and

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \tag{3.11.6}$$

at T_2. By rewriting Equation 3.11.6:

$$\ln A = \ln k_2 + \frac{E_a}{RT_2} \tag{3.11.7}$$

and substitute for $\ln A$ into Equation 3.11.5:

$$\ln k_1 = \ln k_2 + \frac{E_a}{RT_2} - \frac{E_a}{RT_1} \tag{3.11.8}$$

This simplifies to:

$$\ln k_1 - \ln k_2 = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Summary

After observing that many chemical reaction rates depended on the temperature, Arrhenius developed this equation to characterize the temperature-dependent reactions:

$$k = Ae^{\frac{-E_a}{RT}}$$

or

$$\ln k = \ln A - \frac{E_a}{RT}$$

with the following terms:

k: Chemical reaction rate constant

- In unit of s^{-1}(for 1st order rate constant) or $M^{-1}s^{-1}$(for 2nd order rate constant)

A: The pre-exponential factor or frequency factor

- Specifically relates to molecular collision
- Deals with the frequency of molecules that collide in the correct orientation and with enough energy to initiate a reaction.
- *It is a factor that is determined experimentally, as it varies with different reactions.*
- In unit of L $mol^{-1}s^{-1}$ or $M^{-1}s^{-1}$(for 2nd order rate constant) and s^{-1}(for 1st order rate constant)
- Because frequency factor A is related to molecular collision, it is temperature dependent
- Hard to extrapolate pre-exponential factor because lnk is only linear over a narrow range of temperature

E_a: The activation energy is the threshold energy that the reactant(s) must acquire before reaching the transition state.

- Once in the transition state, the reaction can go in the forward direction towards product(s), or in the opposite direction towards reactant(s).
- A reaction with a large activation energy requires much more energy to reach the transition state.
- Likewise, a reaction with a small activation energy doesn't require as much energy to reach the transition state.
- In units of J/mol.
- $-E_a/RT$ resembles the Boltzmann distribution law.

R: The gas constant.

- Its value is 8.314 J/mol K.

T: The absolute temperature at which the reaction takes place.

- In units of Kelvin (K).

Problems

1. Find the activation energy (in kJ/mol) of the reaction if the rate constant at 600K is 3.4 $M^{-1}s^{-1}$ and 31.0 at 750K.
2. Find the rate constant if the temperature is 289K, Activation Energy is 200kJ/mol and pre-exponential factor is 9 $M^{-1}s^{-1}$
3. Find the new rate constant at 310K if the rate constant is 7 $M^{-1}s^{-1}$ at 370K, Activation Energy is 900kJ/mol
4. Calculate the activation energy if the pre-exponential factor is 15 $M^{-1}s^{-1,}$ rate constant is 12$M^{-1}s^{-1}$and it is at 22K
5. Find the new temperature if the rate constant at that temperature is 15$M^{-1}s^{-1}$ while at temperature 389K the rate constant is 7$M^{-1}s^{1,}$ the Activation Energy is 600kJ/mol

Solutions

1. E_a is the factor the question asks to be solved. Therefore it is much simpler to use

$$\ln k = -\frac{E_a}{RT} + \ln A$$

To find E_a, subtract ln A from both sides and multiply by -RT.

This will give us:

$$E_a = \ln A - \ln k)RT$$

2. Substitute the numbers into the equation:

$$lnk = \frac{-(200\times1000\ \text{J})}{(8.314\ \text{J mol}^{-1}\text{K}^{-1})(289\ \text{K})} + \ln 9$$

$k = 6.37X10^{-36}\ M^{-1}s^{-1}$

3. Use the equation $ln(k_1/k_2)=-Ea/R(1/T_1-1/T_2)$

$\ln(7/k_2)$=-[(900 X 1000)/8.314](1/370-1/310)

$k_2=1.788X10^{-24}\ M^{-1}s^{-1}$

4. Use the equation $k = Ae^{-Ea/RT}$

$12 = 15e^{-Ea/(8.314)(22)}$

$Ea = 40.82J/mol$

5. Use the equatioin $ln(k_1/k_2)=-Ea/R(1/T_1-1/T_2)$

$\ln(15/7)$=-[(600 X 1000)/8.314](1/T_1 - 1/389)

$T_1 = 390.6K$

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Contributors and Attributions

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3.12: Kinetics of Catalysis

Learning Objectives

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure **3.12.1**). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.

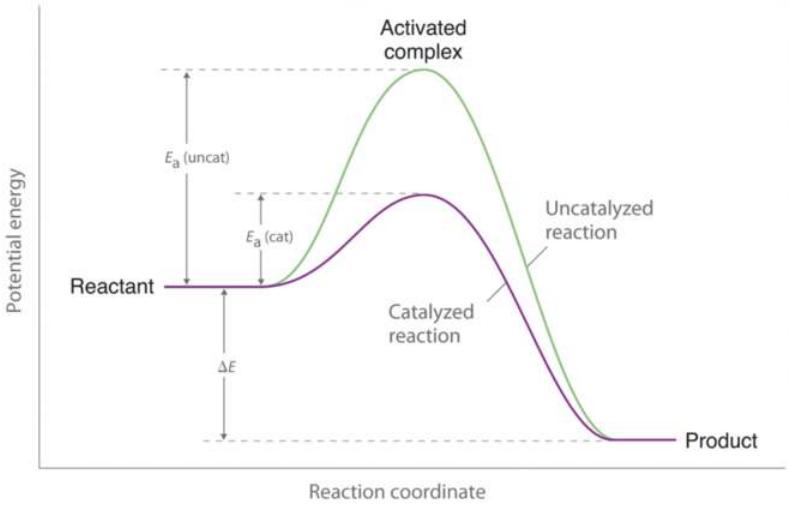


Figure **3.12.1**: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure **3.12.2**, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

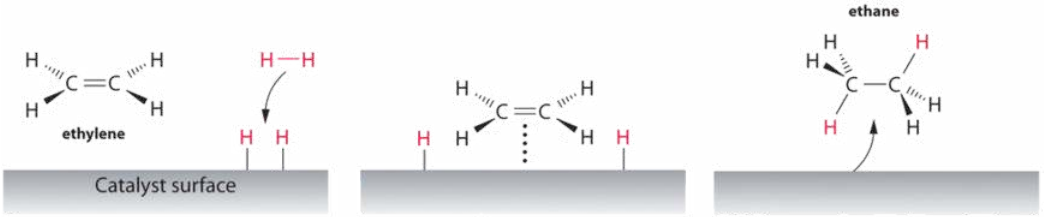


Figure **3.12.2**: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure **3.12.2** shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table **3.12.1**. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

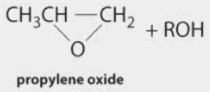
Table **3.12.1**: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$\mathbf{CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O}$	$\mathbf{CH_2{=}CHCN}$ acrylonitrile
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table **3.12.2**), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table **3.12.2**: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	 propylene oxide
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$-(CH_2CH_2-)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure **3.12.3**).



Figure **3.12.3**: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of $\mathbf{H_2O_2}$.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In

homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

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CHAPTER OVERVIEW

4: Chemical Equilibrium

4.1: Prelude to Equilibrium
4.2: Chemical Equilibria
4.3: Equilibrium Constants
4.4: Free Energy and the Equilibrium Constant
4.5: Equilibrium Calculations
4.6: Precipitation and Dissolution
4.7: Solubility Products
4.8: Shifting Equilibria - Le Chatelier's Principle

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4.1: Prelude to Equilibrium

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

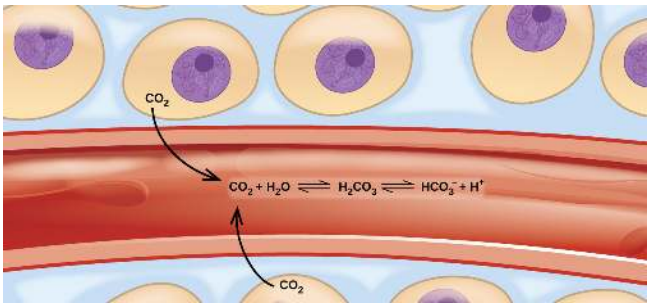


Figure **4.1.1**: Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

An image depicts three tan squares, lying side-by-side along the upper left corner. Two of the same squares also lie side-by-side in the lower right corner. Each square has a black dot in the center. One of the squares is labeled, “C O subscript 2,” and has a double-headed arrow pointing from it to a red tube-like structure that runs between the squares across the image from the upper right to the lower left. This arrow is labeled, “C O subscript 2 dissolved in plasma.” The red tube has two round red shapes in it, and the upper one is labeled, “C O subscript 2 carried in red blood cells.” The gaps between the squares and the red tube are colored light blue. One of the squares along the top of the image is labeled, “C O subscript 2,” and is connected by a double-headed arrow to an equation in the red tube that is labeled, “C O subscript 2, a plus sign, H subscript 2 O, right-facing arrow, H subscript 2 C O subscript 3, right-facing arrow, H C O subscript 3 superscript negative sign, plus sign, H superscript positive sign.” The compound “H C O subscript 3 superscript negative sign” is then connected by a double-headed arrow to the space in the red tube and is labeled, “H C O subscript 3 superscript negative sign dissolved in plasma as carbonic acid.”

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid ($\mathbf{HCO_3^-}$) (Figure **4.1.1**). Human physiology is adapted to the amount of ionized products produced by this reaction ($\mathbf{HCO_3^-}$ and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

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4.2: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$\mathrm{N_2O_4(g)} \mhchemrightleftharpoons 2\,\mathrm{NO_2(g)} \tag{4.2.1}$$

The color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 4.2.1).

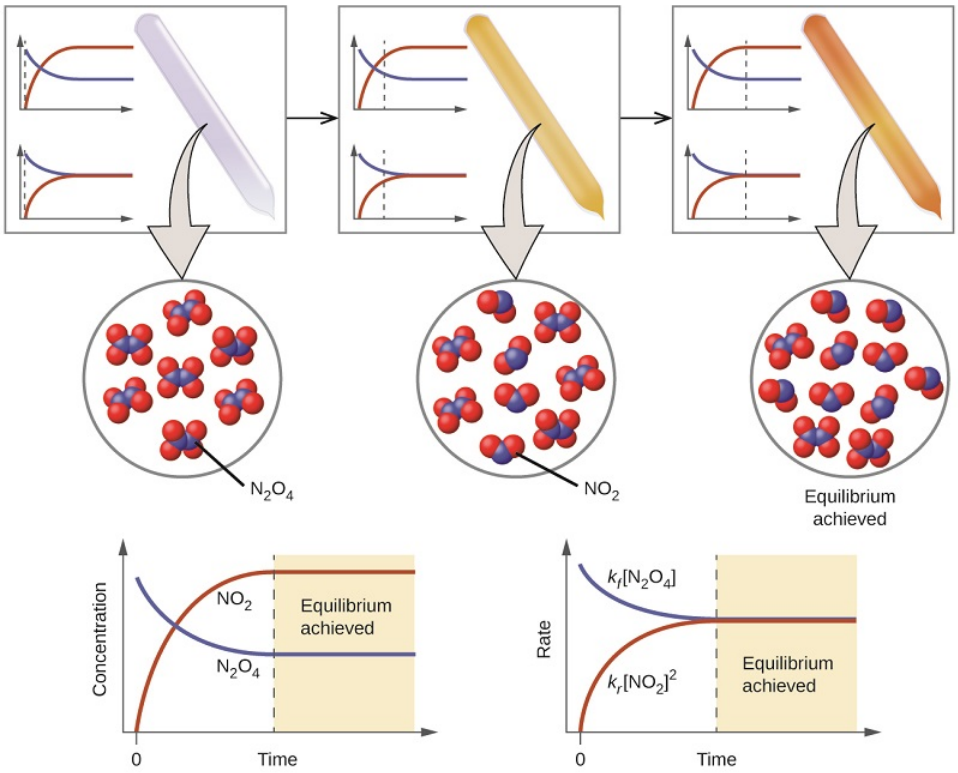


Figure **4.2.1**: A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

A three-part diagram is shown. At the top of the diagram, three beakers are shown, and each one contains a sealed tube. The tube in the left beaker is full of a colorless gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows seven particles, each composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The tube in the middle beaker is full of a light brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows nine particles, five of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining four are composed of two red spheres connected to a blue sphere. The tube in the right beaker is full of a brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows eleven particles, three of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining eight are composed of two red spheres connected to a blue sphere. At the bottom of the image are two graphs. The left graph has a y-axis labeled, “Concentration,” and an x-axis labeled, “Time.” A red line labeled, “N O subscript 2,” begins in the bottom left corner of the graph at a point labeled, “0,” and rises near the highest point on the y-axis before it levels off and becomes horizontal. A blue line labeled, “N subscript 2 O subscript 4,” begins near the highest point on the y-axis and drops below the midpoint of the y-axis before leveling off. The right graph has a y-axis labeled, “Rate,” and an x-axis labeled, “Time.” A red line labeled, “k subscript f, [N subscript 2 O subscript 4],” begins in the bottom left corner of the graph at a point labeled, “0,” and rises near the middle of the y-axis before it levels off and becomes horizontal. A blue line labeled, “k subscript f, [N O subscript 2] superscript 2,” begins near the highest point on the y-axis and drops to the same point on the y-axis as the red line before leveling off. The point where both lines become horizontal is labeled, “Equilibrium achieved.”

The formation of NO_2 from N_2O_4 is a reversible reaction, which is identified by the equilibrium arrow (⇌). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure **4.2.2**).



Figure 4.2.2: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 4.2.1.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 4.2.1 shows the reaction:

$$\mathrm{N_2O_4\,(g)} \mhchemrightleftharpoons \mathrm{2\,NO_2\,(g)} \tag{4.2.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 4.2.1, the rate of the forward reaction

$$\mathrm{2\,NO_2\,(g)} \rightarrow \mathrm{N_2O_4\,(g)} \tag{4.2.3}$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4\,(g)} \rightarrow \mathrm{2\,NO_2\,(g)} \tag{4.2.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$\mathrm{H_2SO_4\,(l) + CaCO_3\,(s)} \rightarrow \mathrm{CO_2\,(g) + H_2O\,(l) + CaSO_4\,(aq)}$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$\mathrm{CO_2\,(aq) + H_2O\,(l)} \mhchemrightleftharpoons \mathrm{H_2CO_3\,(aq)} \mhchemrightleftharpoons \mathrm{HCO_3^-\,(aq) + H^+\,(aq)}$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in

the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure 4.2.3). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."



Figure 4.2.3: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

A bottle of soda sitting on the ground is shown with a large amount of fizz-filled liquid spewing out of the top.

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \mhchemrightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 4.2.4 shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.



Figure 4.2.4: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: Bromine [images-of-elements.com]).

A glass container is shown that is filled with an orange-brown gas and a small amount of dark orange liquid.

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

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4.3: Equilibrium Constants

Learning Objectives

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol ($\rightleftharpoons$) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$m\mathrm{A} + n\mathrm{B} + \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{4.3.1}$$

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \tag{4.3.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)} \tag{4.3.3}$$

is given by this expression:

$$Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{4.3.4}$$

Example 4.3.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,\mathrm{O}_{2(g)} \rightleftharpoons 2\,\mathrm{O}_{3(g)}$
b. $\mathrm{N}_{2(g)} + 3\,\mathrm{H}_{2(g)} \rightleftharpoons 2\,\mathrm{NH}_{3(g)}$
c. $4\,\mathrm{NH}_{3(g)} + 7\,\mathrm{O}_{2(g)} \rightleftharpoons 4\,\mathrm{NO}_{2(g)} + 6\,\mathrm{H_2O}_{(g)}$

Solution

a. $Q_c = \dfrac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3}$
b. $Q_c = \dfrac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$
c. $Q_c = \dfrac{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}$

Exercise 4.3.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,\mathrm{SO}_2(g) + \mathrm{O}_2(g) \rightleftharpoons 2\,\mathrm{SO}_3(g)$
b. $\mathrm{C_4H_8}(g) \rightleftharpoons 2\,\mathrm{C_2H_4}(g)$
c. $2\,\mathrm{C_4H_{10}}(g) + 13\,\mathrm{O}_2(g) \rightleftharpoons 8\,\mathrm{CO}_2(g) + 10\,\mathrm{H_2O}(g)$

Answer a

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Answer b

$$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

Answer c

$$Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 4.3.1). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

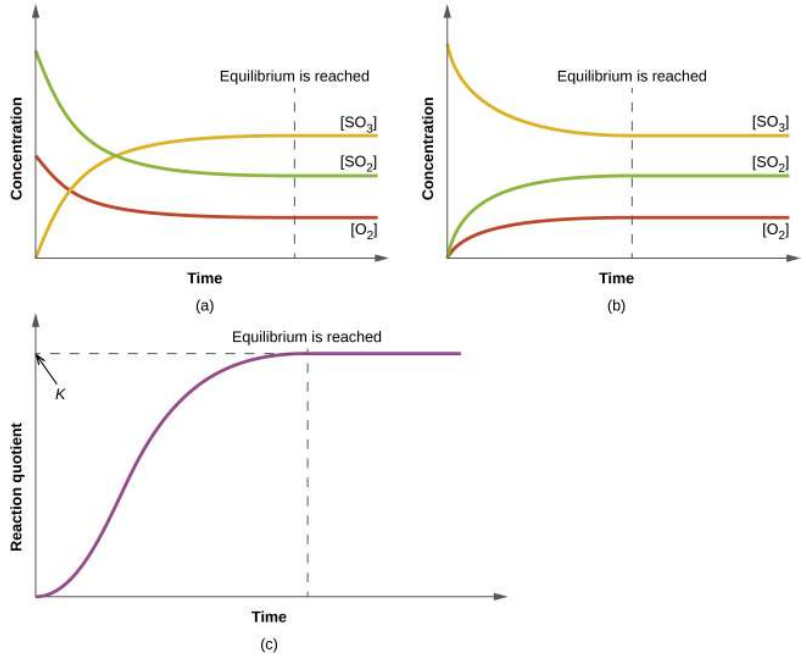


Figure 4.3.1: (a) The change in the concentrations of reactants and products is depicted as the $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

Three graphs are shown and labeled, “a,” “b,” and “c.” All three graphs have a vertical dotted line running through the middle labeled, “Equilibrium is reached.” The y-axis on graph a is labeled, “Concentration,” and the x-axis is labeled, “Time.” Three curves are plotted on graph a. The first is labeled, “[S O subscript 2];” this line starts high on the y-axis, ends midway down the y-axis, has a steep initial slope and a more gradual slope as it approaches the far right on the x-axis. The second curve on this graph is labeled, “[O subscript 2];” this line mimics the first except that it starts and ends about fifty percent lower on the y-axis. The third curve is the inverse of the first in shape and is labeled, “[S O subscript 3].” The y-axis on graph b is labeled, “Concentration,” and the x-axis is labeled, “Time.” Three curves are plotted on graph b. The first is labeled, “[S O subscript 2];” this line starts low on the y-axis, ends midway up the y-axis, has a steep initial slope and a more gradual slope as it approaches the far right on the x-axis. The second curve on this graph is labeled, “[O subscript 2];” this line mimics the first except that it ends about fifty percent lower on the y-axis. The third curve is the inverse of the first in shape and is labeled, “[S O subscript 3].” The y-axis on graph c is labeled, “Reaction Quotient,” and the x-axis is labeled, “Time.” A single curve is plotted on graph c. This curve begins at the bottom of the y-axis and rises steeply up near the top of the y-axis, then levels off into a horizontal line. The top point of this line is labeled, “k.”

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant (K) of the reaction at that temperature. As for the reaction quotient,

when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y\ldots}{[\mathrm{A}]^m[\mathrm{B}]^n\ldots} \tag{4.3.5}$$

This equation is a mathematical statement of the law of mass action: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 4.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)}$$

When 0.10 mol $\mathrm{NO_2}$ is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, [NO_2] = 0.016 M and [N_2O_4] = 0.042 M.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[\mathrm{NO_2}] = \dfrac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\ M$, and [$N_2O_4$] = 0 *M*. Thus,

$$Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from activities instead of molar concentrations, and so K_c values are truly unitless.

Exercise 4.3.2

For the reaction

$$2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$$

the concentrations at equilibrium are [SO_2] = 0.90 *M*, [O_2] = 0.35 *M*, and [SO_3] = 1.1 *M*. What is the value of the equilibrium constant, K_c?

Answer

K_c = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 4.3.2 illustrate this. When

heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 0.640 \quad T = 800^\circ C \tag{4.3.6}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 4.3.2 when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

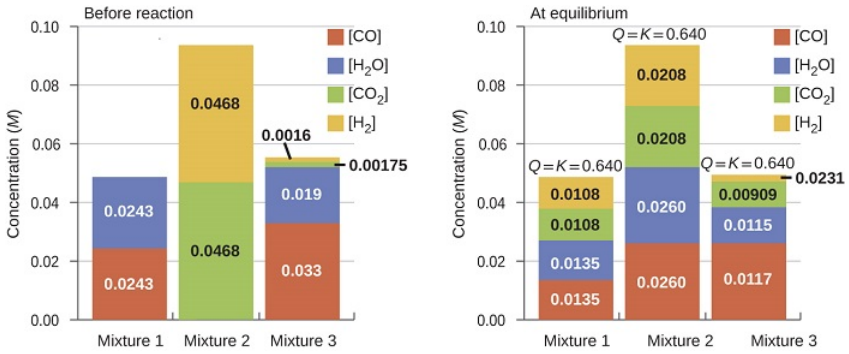


Figure 4.3.2: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 4.3.6).

Two sets of bar graphs are shown. The left is labeled, “Before reaction,” and the right is labeled, “At equilibrium.” Both graphs have y-axes labeled, “Concentration (M),” and three bars on the x-axes labeled, “Mixture 1,” “Mixture 2,” and “Mixture 3.” The y-axis has a scale beginning at 0.00 and ending at 0.10, with measurement increments of 0.02. The bars on the graphs are color coded and a key is provided with a legend. Red is labeled, “C O;” blue is labeled, “H subscript 2 O;” green is labeled, “C O subscript 2,” and yellow is labeled, “H subscript 2.” The graph on the left shows the red bar for mixture one just above 0.02 and the blue bar near 0.05. For mixture two, the green bar is near 0.05, and the yellow bar is near 0.09. For mixture 3, the red bar is near 0.01, the blue bar is slightly above that with green and yellow topping it off at 0.02. On the right graph, the bar for mixture one shows the red bar slightly above 0.01, the blue bar stacked on it rising slightly above 0.02, the green rising near 0.04, and the yellow bar reaching near 0.05. A label above this bar reads, “Q equals 0.640.” The bar for mixture two shows the red bar slightly above 0.02, the blue bar stacked on it rising near 0.05, the green rising near 0.07, and the yellow bar reaching near 0.10. A label above this bar reads “Q equals 0.640.” The bar for mixture three shows the red bar near 0.01, the blue bar stacked on it rising slightly above 0.01, the green rising near 0.02, and the yellow bar reaching 0.02. A label above this bar reads “Q equals 0.640”.

Example 4.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

with $K_c = 0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactant/Products for Three Experiments

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 M	0.011 M	0.0094 M
$[H_2O]_i$	0.0203 M	0.0011 M	0.0025 M
$[CO_2]_i$	0.0040 M	0.037 M	0.0015 M
$[H_2]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

? Exercise 4.3.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$$

Answer a

Q_c = 6.45 × 10^3, shifts right.

Answer b

Q_c = 0.12, shifts left.

Answer c

Q_c = 0, shifts right

In Example 4.3.2, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a solute's activity and its molar concentration are roughly equal.

- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

As a consequence of this last two aspects, Q_c and K_c expressions do not contain terms for solids or liquids or solvents in dilute solutions (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$\mathrm{C_2H_2}(aq) + 2\,\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \tag{4.3.7}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{C_2H_2Br_4}]}{[\mathrm{C_2H_2}][\mathrm{Br_2}]^2} \tag{4.3.8}$$

Example 2

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{4.3.9}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}][\mathrm{I^-}]} \tag{4.3.10}$$

Example 3

$$\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H_3O^+}(aq) \rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\,\mathrm{H_2O}(l) \tag{4.3.11}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{Hg^{2+}}]^2[\mathrm{HNO_2}]}{[\mathrm{Hg_2^{2+}}][\mathrm{NO_3^-}][\mathrm{H_3O^+}]^3} \tag{4.3.12}$$

Example 4

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \tag{4.3.13}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]} \tag{4.3.14}$$

Example 5

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{4.3.15}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]} \tag{4.3.16}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, it is assigned an activity of 1, and thus **does not** appear explicitly as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{4.3.17}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{C_2H_4}][\mathrm{H_2}]}{[\mathrm{C_2H_6}]} \tag{4.3.18}$$

Example 2

$$3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{O_3}(g) \tag{4.3.19}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3} \tag{4.3.20}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{4.3.21}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} \tag{4.3.22}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{4.3.23}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{CO_2}]^3[\mathrm{H_2O}]^4}{[\mathrm{C_3H_8}][\mathrm{O_2}]^5} \tag{4.3.24}$$

Note that the concentration of $\mathrm{H_2O}_{(g)}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where *M* is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{4.3.25}$$

$$P = \left(\frac{n}{V}\right)RT \tag{4.3.26}$$

$$= MRT \tag{4.3.27}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{4.3.28}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{4.3.29}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{C_2H_6}$ is the partial pressure of C_2H_6; P_{H_2}, the partial pressure of H_2; and $P_{C_2H_6}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}} \tag{4.3.30}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{4.3.31}$$

with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \tag{4.3.32}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \tag{4.3.33}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \tag{4.3.34}$$

$$= K_c (RT)^{(x+y)-(m+n)} \tag{4.3.35}$$

$$= K_c (RT)^{\Delta n} \tag{4.3.36}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n} \tag{4.3.37}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$, we have

$$\Delta n = (x + y) - (m + n) \tag{4.3.38}$$

Example 4.3.4: Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$
b. $\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$
c. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g)$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1 = K_c\,(RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^0 = K_c$$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-2} = \frac{K_c}{(RT)^2}$$

d) $K_P = K_c\,(\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

? Exercise 4.3.4

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
b. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$
c. $\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g)$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$\mathrm{CH_3OH}(g) \rightleftharpoons \mathrm{CO}(g) + 2\,\mathrm{H_2}(g)$$

What would be the value of K_P at this temperature?

Answer a

$K_P = K_c\,(RT)^{-1}$

Answer b

$K_P = K_c\,(RT)$

Answer c

$K_P = K_c\,(RT)$;

Answer d

160 or 1.6×10^2

Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$\mathrm{PbCl_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \tag{4.3.39}$$

with associated equilibrium constant

$$K_c = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \tag{4.3.40}$$

Example 1

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{4.3.41}$$

with associated equilibrium constant

$$K_c = \frac{1}{[\mathrm{CO_2}]} \tag{4.3.42}$$

Example 1

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{4.3.43}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{CS_2}]}{[\mathrm{S}]^2} \tag{4.3.44}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g) \tag{4.3.45}$$

with associated equilibrium constant

$$K_c = [\mathrm{Br_2}] \tag{4.3.46}$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using **partial pressures** instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{4.3.47}$$

with associated equilibrium constant

$$K_P = \frac{1}{P_{\mathrm{CO_2}}} \tag{4.3.48}$$

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{4.3.49}$$

with associated equilibrium constant

$$K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{4.3.50}$$

Summary

For any reaction that is at equilibrium, the reaction quotient *Q* is equal to the equilibrium constant *K* for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal *K* (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

Key Equations

- $Q = \dfrac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \dfrac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_P = K_c\,(RT)^{\Delta n}$

Glossary

equilibrium constant (*K*)
value of the reaction quotient for a system at equilibrium

heterogeneous equilibria
equilibria between reactants and products in different phases

homogeneous equilibria
equilibria within a single phase

K_c
: equilibrium constant for reactions based on concentrations of reactants and products

K_P
: equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

law of mass action
: when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (*Q*)
: ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

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4.4: Free Energy and the Equilibrium Constant

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:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. 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 **4.4.1** summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table **4.4.1**: 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 are assessing 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^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also 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^o 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 follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{4.4.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 4.4.1 simplifies to

$$\Delta G = V\Delta P \tag{4.4.2}$$

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 4.4.2 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):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{4.4.3}$$

$$= nRT\frac{\Delta P}{P} \tag{4.4.4}$$

$$= nRT\ln\left(\frac{P_f}{P_i}\right) \tag{4.4.5}$$

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:

$$G - G^\circ = nRT \ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{4.4.6}$$

As you will soon discover, Equation 4.4.6 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:

$$aA + bB \rightleftharpoons cC + dD \tag{4.4.7}$$

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:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{4.4.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{4.4.9}$$

Substituting Equation 4.4.6 for each term into Equation 4.4.9,

$$\begin{aligned}\Delta G = &[(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] \\ &- [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)]\end{aligned}$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) \tag{4.4.10}$$

$$= \Delta G^\circ + RT \ln Q \tag{4.4.11}$$

where ΔG^o 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:

$$0 = \Delta G^o + RT \ln K_p \tag{4.4.12}$$

$$\Delta G^o = -RT \ln K_p \tag{4.4.13}$$

If the products and reactants are in their standard states and $\Delta G^o < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^o > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^o = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

Example 4.4.1

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

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

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm, and
- $T = 100^oC$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 4.4.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 4.4.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 4.4.11. 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 Because ΔG^o is −, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 4.4.11,

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right]$$
$$= -32.7 \text{ kJ} + (-44 \text{ kJ})$$
$$= -77 \text{ kJ/mol of } N_2$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 4.4.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o 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. The reaction will proceed in the forward direction to reach equilibrium.

✓ Example 4.4.2

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 4.4.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 4.4.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 4.4.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 4.4.13,

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

$$\frac{-\Delta G^\circ}{RT} = \ln K_p$$

Inserting the value of ΔG^o 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 product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 4.4.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is −70.5 kJ/mol of O_2.

Answer

2.3×10^{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. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{4.4.14}$$

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 4.4.13 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{4.4.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 4.4.15 for the difference between K_p and K.

Non-Ideal Behavior

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 Equation 4.4.15 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG^o influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4.4.16}$$

$$= -RT \ln K \tag{4.4.17}$$

Notice that K becomes larger as ΔS^o 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^o 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 entropy and seek the lowest energy state possible.*



Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 4.4.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{4.4.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), 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 4.4.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 4.4.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o 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^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. 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 4.4.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4.4.19}$$

Thus calculating ΔH^o 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^o and ΔS^o are independent of temperature.

Example 4.4.4

The equilibrium constant for the formation of $\mathbf{NH_3}$ from $\mathbf{H_2}$ and $\mathbf{N_2}$ at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example **4.4.3**. What is K_p at 500°C? (Use the data from Example **4.4.1**.)

Given: balanced chemical equation, $\Delta H°°$, 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 4.4.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of $\Delta H°$ 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 4.4.19 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise 4.4.4

In the exercise in Example **4.4.3**, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the $\Delta H_f°$ values in the exercise in Example **4.4.1** to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}



The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial

pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G^o < 0$, then K > 1, and products are favored over reactants at equilibrium. Conversely, if $\Delta G^o > 0$, then K < 1, and reactants are favored over products at equilibrium. If $\Delta G^o = 0$, then K=1, and neither reactants nor products are favored 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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4.5: Equilibrium Calculations

Learning Objectives

- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$$

If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 M, the change in the N_2 concentration, $\Delta[N_2]$, the final concentration minus the initial concentration, is 0.11 M. The change is positive because the concentration of N_2 increases.

The change in the H_2 concentration, $\Delta[H_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

$$\begin{aligned}\Delta[\mathrm{H_2}] &= 3 \times \Delta[\mathrm{N_2}] \\ &= 3 \times (0.11\ M) \\ &= 0.33\ M\end{aligned}$$

The change in concentration of NH_3, $\Delta[NH_3]$, is twice that of $\Delta[N_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is negative because the concentration of ammonia *decreases* as it decomposes.

$$\begin{aligned}\Delta[\mathrm{NH_3}] &= -2 \times \Delta[\mathrm{N_2}] \\ &= -2 \times (0.11\ M) \\ &= -0.22\ M\end{aligned}$$

We can relate these relationships directly to the coefficients in the equation

$$2\,\mathrm{NH_3}(g) \quad \mathrm{N_2}(g) \quad 3\,\mathrm{H_2}(g) \tag{4.5.1}$$

$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] \quad \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \tag{4.5.2}$$

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2, we could represent it by the symbol x.

$$\Delta[\mathrm{N_2}] = x$$

The changes in the other concentrations would then be represented as:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$

$$\Delta[NH_3] = -2 \times \Delta[N_2] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \tag{4.5.3}$$
$$-2x \qquad x \qquad 3x \tag{4.5.4}$$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 4.5.1: Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{4.5.5}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{4.5.6}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{4.5.7}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad x \tag{4.5.8}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{4.5.9}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{4.5.10}$$

Solution

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{4.5.11}$$
$$x \qquad 2x \qquad -x \tag{4.5.12}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{4.5.13}$$
$$-x \qquad -x \qquad x \tag{4.5.14}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{4.5.15}$$
$$x \qquad 5x \qquad -3x \qquad -4x \tag{4.5.16}$$

Exercise 4.5.1

Complete the changes in concentrations for each of the following reactions:

(a)

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \tag{4.5.17}$$
$$\_\_\_\_ \qquad x \qquad \_\_\_\_ \tag{4.5.18}$$

(b)

$$C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g) \tag{4.5.19}$$
$$\_\_\_\_ \qquad -2x \tag{4.5.20}$$

(c)

$$4\,NH_3(g) + 7\,H_2O(g) \rightleftharpoons 4\,NO_2(g) + 6\,H_2O(g) \tag{4.5.21}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{4.5.22}$$

Answer a

$2x$, x, $-2x$

Answer b

x, $-2x$

Answer c

$4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant**. If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations**. If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations**. If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_P, K_P, and partial pressure. We will look at solving each of these cases in sequence.

Calculation of an Equilibrium Constant

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

Example **4.5.1** showed us how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE table —for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the initial concentrations of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the change that occurs as the system shifts toward equilibrium—do not forget to consider the reaction stoichiometry as described in a previous section of this chapter. The last row contains the concentrations once equilibrium has been reached.

Example 4.5.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

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

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2.

	I_2	+ I^- ⇌	I_3^-
Initial concentration (M)	1.000×10^{-3}	1.000×10^{-3}	0
Change (M)	$-x$	$-x$	$+x$
Equilibrium concentration (M)	$1.000 \times 10^{-3} - x$	$1.000 \times 10^{-3} - x$	x

Since the equilibrium concentration of I_2 is given, we can solve for x. At equilibrium the concentration of I_2 is 6.61×10^{-4} M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$

$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$

$$= 3.39 \times 10^{-4}\ M$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2 + I^- $\rightleftharpoons$ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x = -3.39 \times 10^{-4}$	$-x$	$+x$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

We now calculate the value of the equilibrium constant.

$$K_c = Q_c = \frac{[I3-]}{[I2][I-]}$$

$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

? Exercise 4.5.2

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Answer

$K_c = 4$

Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

✓ Example 4.5.3: Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, $[N_2]$ = 0.036 mol/L and $[O_2]$ 0.0089 mol/L.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_c = Q_c = \frac{[NO]^2}{[N2][O2]}$$

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$Q_c = \frac{[NO]^2}{[N2][O2]}$$

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

$$= 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

? Exercise 4.5.3

The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer

1.53 mol/L

Calculation of Changes in Concentration

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
   - Write a balanced chemical equation for the reaction.
   - If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
   - Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol *x* and express the other changes in terms of the smallest change.
   - Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
   - Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for *x*, and check any assumptions used to find *x*.
   - Calculate the equilibrium concentrations.
4. Check the arithmetic.
   - Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.

In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example 4.5.4: Calculation of Concentration as a Reaction Equilibrates

Under certain conditions, the equilibrium constant for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 *M*?

Solution

Use the stepwise process described earlier.

1. The balanced equation for the decomposition of PCl_5 is

$$\mathbf{PCl_5}(g) \rightleftharpoons \mathbf{PCl_3}(g) + \mathbf{Cl_2}(g)$$

Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.

- Let us represent the increase in concentration of PCl_3 by the symbol *x*. The other changes may be written in terms of *x* by considering the coefficients in the chemical equation.

$$\mathbf{PCl_5}(g) \rightleftharpoons \mathbf{PCl_3}(g) + \mathbf{Cl_2}(g) \tag{4.5.23}$$
$$-x \qquad x \qquad x \tag{4.5.24}$$

- The changes in concentration and the expressions for the equilibrium concentrations are:

	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	$0 + x = x$	$0 + x = x$

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M), Change (M), Equilibrium concentration (M). The second column has the header, “P C l subscript 5 equilibrium arrow P C l subscript 3 plus C l subscript 2.” Under the second column is a subgroup of three rows and three columns. The first column has the following: 1.00, negative x, 1.00 minus x. The second column has the following: 0, positive x, 0 plus x equals x. The third column has the following: 0, positive x, 0 plus x equals x.

- Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl3][Cl2]}{[PCl5]} = 0.0211$$
$$= \frac{(x)(x)}{(1.00 - x)}$$

This equation contains only one variable, *x*, the change in concentration. We can write the equation as a quadratic equation and solve for *x* using the quadratic formula.

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$
$$0.0211(1.00 - x) = x^2$$
$$x^2 + 0.0211x - 0.0211 = 0$$

An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for *x*:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for *a*, *b*, and *c* yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

Hence

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

Quadratic equations often have two different solutions, one that is physically possible and one that is physically impossible (an extraneous root). In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, x = 0.135 M.

The equilibrium concentrations are

$[PCl_5] = 1.00 - 0.135 = 0.87\ M$
$[PCl_3] = x = 0.135\ M$
$[Cl_2] = x = 0.135\ M$

- Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl3][Cl2]}{[PCl5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations check.

? Exercise 4.5.4A

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 M in CH_3CO_2H, 0.15 M in C_2H_5OH, 0.40 M in $CH_3CO_2C_2H_5$, and 0.40 M in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Answer

$[CH_3CO_2H]$ = 0.36 M, $[C_2H_5OH]$ = 0.36 M, $[CH_3CO_2C_2H_5]$ = 0.17 M, $[H_2O]$ = 0.17 M

? Exercise 4.5.4B

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, [HI] = 1.88 M

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products.

Consider the ionization of 0.150 M HA, a weak acid.

$$\mathrm{HA}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{A^-}(aq) \quad K_c = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the "all reactant" starting point. Using *x* for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	$\mathrm{HA}(aq) \rightleftharpoons$	$\mathrm{H^+}(aq)$	+ $\mathrm{A^-}(aq)$
Initial concentration (*M*)	0.150	0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.150 − *x*	*x*	*x*

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, "H A (a q) equilibrium arrow H superscript plus sign (a q) plus A subscript negative sign (a q)." Under the second column is a subgroup of three columns and three rows. The first column has the following: 0.150, negative x, 0.150 minus x. The second column has the following: 0, x, x. The third column has the following: 0, x, x.

Setting up and solving the quadratic equation gives

$$K_c = \frac{[H+][A-]}{[HA]} = \frac{(x)(x)}{(0.150-x)} = 6.80 \times 10^{-4}$$
$$x^2 + 6.80 \times 10^{-4}x - 1.02 \times 10^{-4} = 0$$
$$x = -6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}(2)(1)$$
$$x = 0.00977\ M \text{ or } -0.0104\ M$$

Using the positive (physical) root, the equilibrium concentrations are

$$[\mathrm{HA}] = 0.150 - x = 0.140\ M$$
$$[\mathrm{H^+}] = [\mathrm{A^-}] = x = 0.00977\ M$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the "all product" starting point. Assuming all of the HA ionizes gives

$$[\mathrm{HA}] = 0.150 - 0.150 = 0\ M$$
$$[\mathrm{H^+}] = 0 + 0.150 = 0.150\ M$$
$$[\mathrm{A^-}] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and "*y*" to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	$\mathrm{HA}(aq) \rightleftharpoons$	$\mathrm{H^+}(aq)$	+ $\mathrm{A^-}(aq)$
Initial concentration (*M*)	0	0.150	0.150
Change (*M*)	+*y*	−*y*	−*y*
Equilibrium concentration (*M*)	*y*	0.150 − *y*	0.150 − *y*

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, "H A (a q) equilibrium arrow H superscript plus sign (a q) plus A subscript negative sign (a q)." Under the second column is a subgroup of three columns and three rows. The first column has the following: 0, positive y, y. The second column has the following: 0.150, negative y, 0.150 minus y. The third column has the following: 0.150, negative y, and 0.150 minus y.

Setting up and solving the quadratic equation gives

$$K_c = \frac{[H+][A-]}{[HA]} = \frac{(0.150-y)(0.150-y)}{(y)} = 6.80 \times 10^{-4}$$
$$6.80 \times 10^{-4}y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$

$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$

$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$$y = 0.160\ M \text{ or } y = 0.140\ M$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[\mathrm{HA}] = y = 0.140\ M$$
$$[\mathrm{H^+}] = 0.150 - y = 0.010\ M$$
$$[\mathrm{A^-}] = 0.150 - y = 0.010\ M$$

Thus, the two approaches give the same results (to three *decimal places*), and show that *both* starting points lead to the same equilibrium conditions. The "all reactant" starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the "all product" starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts "close" to equilibrium will require only a "small" change in conditions (x) to reach equilibrium.

Recall that a small K_c means that very little of the reactants form products and a large K_c means that most of the reactants form products. If the system can be arranged so it starts "close" to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example 4.5.5: Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CN^-}(aq) \quad K_c = 4.9 \times 10^{-10}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

	$\mathrm{HCN}(aq) \rightleftharpoons$	$\mathrm{H^+}(aq)$	+ $\mathrm{CN^-}(aq)$
Initial concentration (M)	0.15	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.15 - x$	x	x

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, "H C N (a q) equilibrium arrow H superscript plus sign (a q) plus C N subscript negative sign (a q)." Under the second column is a subgroup of three columns and three rows. The first column has the following: 0.15, negative x, 0.15 minus x. The second column has the following: 0, x, x. The third column has the following: 0, x, x.

The exact solution may be obtained using the quadratic formula with

$$K_c = \frac{(x)(x)}{0.15 - x}$$

solving

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

$$x = 8.56 \times 10^{-6}\ M\ (3\ \text{sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2\ \text{sig. figs.})$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}\ M$ and $[HCN] = 0.15 - x = 0.15\ M$.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, x must be small compared to 0.15 M. More formally, if $x \ll 0.15$, then $0.15 - x \approx 0.15$. If this assumption is true, then it simplifies obtaining x

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF $(0.15 - x) \approx 0.15\ M$, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

? Exercise 4.5.5

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_c = 1.8 \times 10^{-5}$$

Assume that x is much less than 0.25 M and calculate the error in your assumption.

Answer

$[OH^-] = [NH_4^+] = 0.0021\ M$; $[NH_3] = 0.25\ M$, error = 0.84%

The second example requires that the original information be processed a bit, but it still can be solved using a small x approximation.

✔ Example 4.5.6: Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \quad K_c = 5.0 \times 10^{13} = \frac{[Cu(NH3)4^2+]}{[Cu^2 + (aq)][NH3]^4}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 M NH_3 what are the concentrations when the system comes to equilibrium?

Solution The initial concentration of copper(II) is 0.010 M. The equilibrium constant is very large so it would be better to start with as much product as possible because “all products” is much closer to equilibrium than “all reactants.” Note that Cu^{2+} is the limiting reactant; if all 0.010 M of it reacts to form product the concentrations would be

$$[Cu^{2+}] = 0.010 - 0.010 = 0\ M$$

$$[Cu(NH_3)_4{}^{2+}] = 0.010\ M$$

$$[NH_3] = 1.00 - 4 \times 0.010 = 0.96\ M$$

Using these "shifted" values as initial concentrations with x as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \rightleftharpoons$	$Cu(NH_3)_4^{2+}(aq)$
Initial concentration (M)	0	0.96	0.010
Change (M)	$+x$	$+4x$	$-x$
Equilibrium concentration (M)	x	$0.96 + 4x$	$0.010 - x$

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following: Initial pressure (M), Change (M), Equilibrium (M). The second column has the header, "C u superscript 2 positive sign (a q) plus 4 N H subscript 3 (a q) equilibrium arrow C u (N H subscript 3) subscript 4 superscript 2 positive sign (a q)." Under the second column is a subgroup of three columns and three rows. The first column has the following: 0, positive x, x. The second column has the following: 0.96, positive 4 x, 0.96 plus 4 x. The third column has the following: 0.010, negative x, 0.010 minus x.

Since we are starting close to equilibrium, x should be small so that

$$0.96 + 4x \approx 0.96\ M$$

$$0.010 - x \approx 0.010\ M$$

$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$

$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[Cu^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[NH_3] = 0.96 - 4x = 0.96\ M$$
$$[Cu(NH_3)_4^{2+}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (x) was very small. With only a small change required to get to equilibrium, the equation for x was greatly simplified and gave a valid result well within the 5% error maximum.

? Exercise 4.5.6

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 M NH_3 solution?

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$$

with $K_c = 5.5 \times 10^8$.

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (x) of the product shifts left. Calculate the error in your assumption.

Answer

$[Ni(NH_3)_6^{2+}] = 0.25\ M$, $[NH_3] = 0.50\ M$, $[Ni^{2+}] = 2.9 \times 10^{-8}\ M$, error = $1.2 \times 10^{-5}\%$

Summary

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of X is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium.

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4.6: Precipitation and Dissolution

Learning Objectives

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $Ca_5(PO_4)_3(OH)$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Chatelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a solution.

The Solubility Product Constant

Silver chloride is what's known as a sparingly soluble ionic solid (Figure **4.6.1**). Recall from the solubility rules in an earlier chapter that halides of Ag^+ are not normally soluble. However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride:

$$\mathrm{AgCl}(s) \xrightleftharpoons[\text{precipitation}]{\text{dissolution}} \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

This equilibrium, like other equilibria, is dynamic; some of the solid AgCl continues to dissolve, but at the same time, Ag^+ and Cl^- ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.

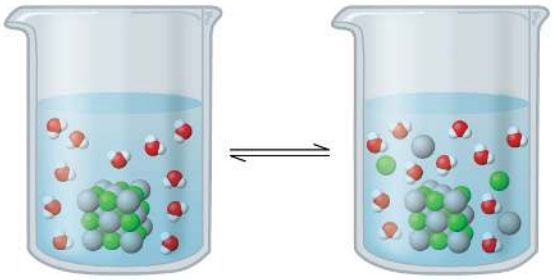


Figure **4.6.1**: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the solubility product (K_{sp}) of the solid. Recall from the chapter on solutions and colloids that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

with

$$K_{sp} = [\mathrm{Ag^+}(aq)][\mathrm{Cl^-}(aq)]$$

When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of the ions, raised to the power of their stoichiometric coefficients. Here, the solubility product constant is equal to Ag^+ and Cl^- when

a solution of silver chloride is in equilibrium with undissolved AgCl. There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore [AgCl] does not appear in the expression for K_{sp}.

Table **4.6.1**: Common Solubility Products by Decreasing Equilibrium Constants

Substance	K_{sp} at 25 °C
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}

Some common solubility products are listed in Table **4.6.1** according to their K_{sp} values, whereas a more extensive compilation of products appears in Table E3. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

✔ Example 4.6.1: Writing Equations and Solubility Products

Write the ionic equation for the dissolution 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

(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

Solution

a. $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \quad K_{sp} = [Ag^+][I^-]$
b. $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \quad K_{sp} = [Ca^{2+}][CO_3^{2-}]$
c. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq) \quad K_{sp} = [Mg^{2+}][OH^-]^2$
d. $Mg(NH_4)PO_4(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) \quad K_{sp} = [Mg^{2+}][NH_4^+][PO_4^{3-}]$
e. $Ca_5(PO_4)_3OH(s) \rightleftharpoons 5\,Ca^{2+}(aq) + 3\,PO_4^{3-}(aq) + OH^-(aq) \quad K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

? Exercise 4.6.1

Write the ionic equation for the dissolution 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

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \quad K_{sp} = [Ba^{2+}][SO_4^{2-}]$

Answer b

$$Ag_2SO_4(s) \rightleftharpoons 2\,Ag^+(aq) + SO_4{}^{2-}(aq) \quad K_{sp} = [Ag^+]^2[SO_4{}^{2-}]$$

Answer c

$$Al(OH)_3(s) \rightleftharpoons Al^{2+}(aq) + 3\,OH^-(aq) \quad K_{sp} = [Al^{3+}][OH^-]^3$$

Answer d

$$Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^-(aq) + Cl^-(aq) \quad K_{sp} = [Pb^{2+}][OH^-][Cl^-]$$

Now we will extend the discussion of K_{sp} and show how the solubility product constant is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

K_{sp} and Solubility

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$M_pX_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per liter (mol/L), known as its molar solubility.

Example 4.6.2: Calculation of K_{sp} from Equilibrium Concentrations

We began the chapter with an informal discussion of how the mineral fluorite is formed. 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 2.1×10^{-4} *M*; therefore, that of F^- is 4.2×10^{-4} *M*, that is, twice the concentration of Ca^{2+}. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$\begin{aligned} K_{sp} &= [Ca^{2+}][F^-]^2 \\ &= (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 \\ &= 3.7 \times 10^{-11} \end{aligned}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 4.6.2

In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 3.7×10^{-5} *M*. What is the solubility product for $Mg(OH)_2$?

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$

Answer

2.0×10^{-13}

Example 4.6.3: 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 solubility product constant of copper(I) bromide is $\mathbf{6.3 \times 10^{-9}}$.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu^+}(aq) + \mathrm{Br^-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [\mathrm{Cu^+}][\mathrm{Br^-}]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the K_{sp}:

	CuBr ⇌	Cu^+	+ Br^-
Initial concentration (*M*)		0	0
Change (*M*)		*x*	*x*
Equilibrium concentration (*M*)		0 + *x* = *x*	0 + *x* = *x*

At equilibrium:

$$K_{sp} = [\mathrm{Cu^+}][\mathrm{Br^-}]$$
$$6.3 \times 10^{-9} = (x)(x) = x^2$$
$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}$$

Therefore, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Exercise 4.6.3

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

1.2×10^{-8} *M*

Example 4.6.4: Determination of Molar Solubility from K_{sp}, Part II

Determination of Molar Solubility from K_{sp}, Part II The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product constant of calcium hydroxide is 1.3×10^{-6}.

The reaction is:

$$\mathrm{Ca(OH)_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{OH^-}]^2$$

Create an ICE table, leaving the $Ca(OH)_2$ column empty as it is a solid and does not contribute to the K_{sp}:

	$Ca(OH)_2 \rightleftharpoons$	Ca^{2+}	+ $2OH^-$
Initial concentration (*M*)		0	0
Change (*M*)		x	$2x$
Equilibrium concentration (*M*)		$0 + x = x$	$0 + 2x = 2x$

At equilibrium:

$$K_{sp} = [Ca^{2+}][OH^-]^2$$
$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$
$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 6.9 \times 10^{-3}$$

Therefore, the molar solubility of $Ca(OH)_2$ is 6.9×10^{-3} *M*.

Exercise 4.6.4

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer

1.5×10^{-3} *M*

Note that solubility is not always given as a molar value. When the solubility of a compound is given in some unit other than moles per liter, we must convert the solubility into moles per liter (i.e., molarity) in order to use it in the solubility product constant expression. Example **4.6.5** shows how to perform those unit conversions before determining the solubility product equilibrium.

Example 4.6.5: Determination of K_{sp} from Gram Solubility

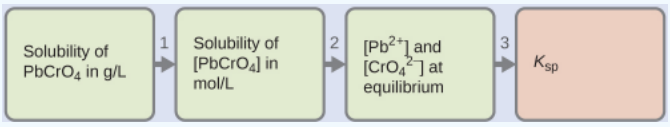
Many of the pigments used by artists in oil-based paints (Figure **4.6.2**) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product equilibrium constant for $PbCrO_4$.



Figure **4.6.2**: 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

We are given the solubility of $PbCrO_4$ in grams per liter. If we convert this solubility into moles per liter, we can find the equilibrium concentrations of Pb^{2+} and CrO_4^{2-}, then K_{sp}:



1. *Use the molar mass of PbCrO4* $\left(\frac{323.2\ \text{g}}{1\ \text{mol}}\right)$ *to convert the solubility of PbCrO4 in grams per liter into moles per liter:*

$$[PbCrO_4] = \frac{4.6 \times 10^{-6}\ \text{g PbCrO}_4}{1\ \text{L}} \times \frac{1\ \text{mol PbCrO}_4}{323.2\ \text{g PbCrO}_4}$$

$$= \frac{1.4 \times 10^{-8}\ \text{mol PbCrO}_4}{1\ \text{L}}$$

$$= 1.4 \times 10^{-8}\ M$$

- *The chemical equation for the dissolution indicates that 1 mol of $PbCrO_4$ gives 1 mol of $Pb^{2+}(aq)$ and 1 mol of $CrO_4^{2-}(aq)$:*
  $PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$

  Thus, both $[Pb^{2+}]$ and $[CrO_4^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

  $[Pb^{2+}] = [CrO_4^{2-}] = 1.4 \times 10^{-8}\ M$
- *Solve.* $K_{sp} = [Pb^{2+}]\ [CrO_4^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

? Exercise 4.6.5

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.46 grams per liter at 20 °C. What is its solubility product?

Answer

2.08×10^{-4}

✔ Example 4.6.6: Calculating the Solubility of Hg_2Cl_2

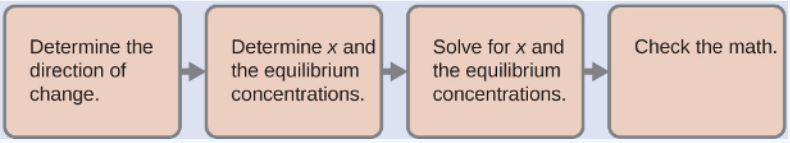
Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), Hg_2^{2+}, and chloride ions, Cl^-. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel is quite insoluble:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq) \quad K_{sp} = 1.1 \times 10^{-18}$$

Calculate the molar solubility of Hg_2Cl_2.

Solution

The molar solubility of Hg_2Cl_2 is equal to the concentration of Hg_2^{2+} ions because for each 1 mol of Hg_2Cl_2 that dissolves, 1 mol of Hg_2^{2+} forms:



1. *Determine the direction of change.* Before any Hg_2Cl_2 dissolves, Q is zero, and the reaction will shift to the right to reach equilibrium.
2. *Determine* x *and equilibrium concentrations.* Concentrations and changes are given in the following ICE table:

	$Hg_2Cl_2 \rightleftharpoons$	Hg_2^{2+} +	$2Cl^-$
Initial concentration (*M*)		0	0
Change (*M*)		x	$2x$
Equilibrium concentration (*M*)		$0 + x = x$	$0 + 2x = 2x$

Note that the change in the concentration of Cl^- ($2x$) is twice as large as the change in the concentration of Hg_2^{2+} (x) because 2 mol of Cl^- forms for each 1 mol of Hg_2^{2+} that forms. Hg_2Cl_2 is a pure solid, so it does not appear in the calculation.

3. *Solve for* x *and the equilibrium concentrations.* We substitute the equilibrium concentrations into the expression for K_{sp} and calculate the value of x:

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$
$$1.1 \times 10^{-18} = (x)(2x)^2$$
$$4x^3 = 1.1 \times 10^{-18}$$
$$x = \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7}\ M$$

So the concentrations are

$$[Hg_2^{2+}] = 6.5 \times 10^{-7}\ M = 6.5 \times 10^{-7}\ M$$
$$[Cl^-] = 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6}\ M$$

The molar solubility of Hg_2Cl_2 is equal to $[Hg_2^{2+}]$, or $6.5 \times 10^{-7}\ M$.

Check the work.

At equilibrium, $Q = K_{sp}$:

$$Q = [Hg_2^{2+}][Cl^-]^2 = (6.5 \times 10^{-7})(1.3 \times 10^{-6})^2 = 1.1 \times 10^{-18}$$

The calculations check.

Exercise 4.6.6

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Answer

$1.2 \times 10^{-3}\ M$

Tabulated K_{sp} values can also be compared to reaction quotients calculated from experimental data to tell whether a solid will precipitate in a reaction under specific conditions: Q equals K_{sp} at equilibrium; if Q is less than K_{sp}, the solid will dissolve until Q equals K_{sp}; if Q is greater than K_{sp}, precipitation will occur at a given temperature until Q equals K_{sp}.

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 1.1×10^{-10}, 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 **4.6.3**).



Figure 4.6.3: The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by "glitzy queen00"/Wikimedia Commons).

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq)$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]$) is equal to the solubility product ($K_{sp} = 4.8 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains $\mathrm{CO_3^{2-}}$ ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and $\mathrm{CO_3^{2-}}$ ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example 4.6.7 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example 4.6.7: 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:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = 8.9 \times 10^{-12}$$

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

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq)$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}] = 0.0537\ M$ and $[OH^-] = 0.0010\ M$. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$Q = [Mg^{2+}][OH^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

Exercise 4.6.7

Use the solubility products in Table E3 to determine whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}] = 0.0001\ M$ and $[HPO_4^{2-}] = 0.001\ M$.

Answer

No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp}

Example 4.6.8: Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-M solution of $AgNO_3$ and a 2.0×10^{-4}-M solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility product is 1.8×10^{-10} (Table E3).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[Ag^+]$ and $[Cl^-]$ are both equal to:

$$\frac{1}{2}(2.0 \times 10^{-4})\ M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, Q, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [Ag^+][Cl^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp}.

Exercise 4.6.8

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^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Answer

No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.07 \times 10^{-2}$

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the

other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Example 4.6.9: 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 4.6.4). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4 \cdot H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} *M*. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4 \cdot H_2O$ begins to precipitate?



Figure 4.6.4: 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 (Table E3):

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8}$$

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $C_2O_4^{2-}$ that is necessary to produce the first trace of solid:

$$Q = K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^{-8}$$

$$(2.2 \times 10^{-3})[C_2O_4^{2-}] = 1.96 \times 10^{-8}$$

$$[C_2O_4^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}$$

A concentration of $[C_2O_4^{2-}] = 8.9 \times 10^{-6}$ *M* is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 4.6.9

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

4.5×10^{-9} *M*

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example 4.6.8—calculation of

the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Example 4.6.10: 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 reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep [Mn^{2+}] equal to 1.8×10^{-6} *M*?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = 2 \times 10^{-13}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is 1.8×10^{-6} *M*. From that, we calculate the pH. At equilibrium:

$$K_{sp} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2$$

or

$$(1.8 \times 10^{-6})[\mathrm{OH^-}]^2 = 2 \times 10^{-13}$$

so

$$[\mathrm{OH^-}] = 3.3 \times 10^{-4}\ M$$

Now we calculate the pH from the pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(3.3 \times 10^{-4}) = 3.48$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 3.48 = 10.52$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of 1.8×10^{-6} *M*; at that concentration or less, the ion will not stain clothing.

Exercise 4.6.10

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 diminished to 1.0×10^{-5} *M* by the addition of $Ca(OH)_2$.

Answer

10.97

Due to their light sensitivity, mixtures of silver halides are used in fiber optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{sp} = 1.6 \times 10^{-10}$), AgBr ($K_{sp} = 5.0 \times 10^{-13}$), and AgI ($K_{sp} = 1.5 \times 10^{-16}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ

by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of selective precipitation, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

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 **4.6.5**). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{2-}) 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 **4.6.5**: 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, known as lime, $Ca(OH)_2$. The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3(OH)$, which then precipitates out of the solution:

$$5\,Ca^{2+} + 3\,PO_4^{3-} + OH^- \mhchemrightleftharpoons Ca_{10}(PO_4)_6 \cdot (OH)_2(s)$$

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.

Selective precipitation can also be used in qualitative analysis. In this method, reagents are added to an unknown chemical mixture in order to induce precipitation. Certain reagents cause specific ions to precipitate out; therefore, the addition of the reagent can be used to determine whether the ion is present in the solution.

Example **4.6.11**: Precipitation of Silver Halides

A solution contains 0.0010 mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

Solution

The two equilibria involved are:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.6 \times 10^{-10}$$

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \quad K_{sp} = 1.5 \times 10^{-16}$$

If the solution contained about *equal* concentrations of Cl^- and I^-, then the silver salt with the smallest K_{sp} (AgI) would precipitate first. The concentrations are not equal, however, so we should find the $[Ag^+]$ at which AgCl begins to precipitate and the $[Ag^+]$ at which AgI begins to precipitate. The salt that forms at the lower $[Ag^+]$ precipitates first.

For AgI: AgI precipitates when Q equals K_{sp} for AgI (1.5×10^{-16}). When $[I^-] = 0.0010\ M$:

$$Q = [Ag^+][I^-] = [Ag^+](0.0010) = 1.5 \times 10^{-16}$$

$$[Ag^+] = \frac{1.5 \times 10^{-16}}{0.0010} = 1.5 \times 10^{-13}$$

AgI begins to precipitate when $[Ag^+]$ is 1.5×10^{-13} *M*.

For AgCl: AgCl precipitates when *Q* equals K_{sp} for AgCl (1.6×10^{-10}). When $[Cl^-] = 0.10$ *M*:

$$Q_{sp} = [Ag^+][Cl^-] = [Ag^+](0.10) = 1.6 \times 10^{-10}$$
$$[Ag^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9}\ M$$

AgCl begins to precipitate when $[Ag^+]$ is 1.6×10^{-9} *M*.

AgI begins to precipitate at a lower $[Ag^+]$ than AgCl, so AgI begins to precipitate first.

? Exercise 4.6.11

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

As we saw when we discussed buffer solutions, the hydronium ion concentration of an aqueous solution of acetic acid decreases when the strong electrolyte sodium acetate, $NaCH_3CO_2$, is added. We can explain this effect using Le Chatelier's principle. The addition of acetate ions causes the equilibrium to shift to the left, decreasing the concentration of H_3O^+ to compensate for the increased acetate ion concentration. This increases the concentration of CH_3CO_2H:

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Because sodium acetate and acetic acid have the acetate ion in common, the influence on the equilibrium is called **the common ion effect.** The common ion effect can also have a direct effect on solubility equilibria. Suppose we are looking at the reaction where silver iodide is dissolved:

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

If we were to add potassium iodide (KI) to this solution, we would be adding a substance that shares a common ion with silver iodide. Le Chatelier's principle tells us that when a change is made to a system at equilibrium, the reaction will shift to counteract that change. In this example, there would be an excess of iodide ions, so the reaction would shift toward the left, causing more silver iodide to precipitate out of solution.

✓ Example 4.6.12: 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

The first thing you should notice is that the cadmium sulfide is dissolved in a solution that contains cadmium ions. We need to use an ICE table to set up this problem and include the $CdBr_2$ concentration as a contributor of cadmium ions:

$$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$$

	$CdS \rightleftharpoons$	Cd^{2+}	+ S^{2-}
Initial concentration (*M*)		0.010	0
Change (*M*)		*x*	*x*
Equilibrium concentration (*M*)		0.010 + *x*	0 + *x* = *x*

This table has two main columns and four rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M), Change (M), and Equilibrium concentration (M). The second column has the header, “C d S equilibrium arrow C d to the second power plus S to the second power superscript negative sign.” Under the second column is a subgroup of three rows and three columns. The first column is blank. The second column has the following: 0.010, x, 0.010 plus x. The third column has the following: 0, x, 0 plus x equals x.

$$K_{sp} = [Cd^{2+}][S^{2-}] = 1.0 \times 10^{-28}$$

$$(0.010 + x)(x) = 1.0 \times 10^{-28}\ x^2 + 0.010x - 1.0 \times 10^{-28} = 0$$

We can solve this equation using the quadratic formula, but we can also make an assumption to make this calculation much simpler. Since the K_{sp} value is so small compared with the cadmium concentration, we can assume that the change between the initial concentration and the equilibrium concentration is negligible, so that $0.010 + x \sim 0.010$. Going back to our K_{sp} expression, we would now get:

$$\begin{gathered} K_{sp} = [Cd^{2+}][S^{2-}] = 1.0 \times 10^{-28} \\ (0.010)(x) = 1.0 \times 10^{-28} \\ x = 1.0 \times 10^{-26} \end{gathered}$$

Therefore, the molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Exercise 4.6.12

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

4×10^{-11}

Summary

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp}, of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions M^{m+} and X^{n-}:

$$M_pX_q(s) \rightleftharpoons pM^{m+}(aq) + qX^{n-}(aq)$$

We write the solubility product expression as:

$$K_{sp} = [M^{m+}]^p[X^{n-}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp}, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions. A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product. A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Chatelier’s principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

Glossary

common ion effect

effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

molar solubility

solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation

process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product (K_{sp})

equilibrium constant for the dissolution of a slightly soluble electrolyte

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4.7: Solubility Products

Solubility Products

Substance	K_{sp} at 25 °C
aluminum	
$Al(OH)_3$	2×10^{-32}
barium	
$BaCO_3$	1.6×10^{-9}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}
$BaSO_4$	2.3×10^{-8}
$BaCrO_4$	8.5×10^{-11}
BaF_2	2.4×10^{-5}
$Ba(OH)_2 \cdot 8H_2O$	5.0×10^{-3}
$Ba_3(PO_4)_2$	6×10^{-39}
$Ba_3(AsO_4)_2$	1.1×10^{-13}
bismuth	
BiO(OH)	4×10^{-10}
BiOCl	1.8×10^{-31}
Bi_2S_3	1×10^{-97}
cadmium	
$Cd(OH)_2$	5.9×10^{-15}
CdS	1.0×10^{-28}
$CdCO_3$	5.2×10^{-12}
calcium	
$Ca(OH)_2$	1.3×10^{-6}
$CaCO_3$	8.7×10^{-9}
$CaSO4 \cdot 2H_2O$	6.1×10^{-5}
$CaC_2O_4 \cdot H_2O$	1.96×10^{-8}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$CaHPO_4$	7×10^{-7}
CaF_2	4.0×10^{-11}
chromium	
$Cr(OH)_3$	6.7×10^{-31}
cobalt	
$Co(OH)_2$	2.5×10^{-16}
CoS(α)	5×10^{-22}
CoS(β)	3×10^{-26}

Substance	K_{sp} at 25 °C
$CoCO_3$	1.4×10^{-13}
$Co(OH)_3$	2.5×10^{-43}
copper	
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
CuI	1.27×10^{-12}
CuSCN	1.6×10^{-11}
Cu_2S	2.5×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}
CuS	8.5×10^{-45}
$CuCO_3$	2.5×10^{-10}
iron	
$Fe(OH)_2$	1.8×10^{-15}
$FeCO_3$	2.1×10^{-11}
FeS	3.7×10^{-19}
$Fe(OH)_3$	4×10^{-38}
lead	
$Pb(OH)_2$	1.2×10^{-15}
PbF_2	4×10^{-8}
$PbCl_2$	1.6×10^{-5}
$PbBr_2$	4.6×10^{-6}
PbI_2	1.4×10^{-8}
$PbCO_3$	1.5×10^{-15}
PbS	7×10^{-29}
$PbCrO_4$	2×10^{-16}
$PbSO_4$	1.3×10^{-8}
$Pb_3(PO_4)_2$	1×10^{-54}
magnesium	
$Mg(OH)_2$	8.9×10^{-12}
$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}
$MgNH_4PO_4$	3×10^{-13}
MgF_2	6.4×10^{-9}
MgC_2O_4	7×10^{-7}
manganese	
$Mn(OH)_2$	2×10^{-13}

Substance	K_{sp} at 25 °C
$MnCO_3$	8.8×10^{-11}
MnS	2.3×10^{-13}
mercury	
$Hg_2O \cdot H_2O$	3.6×10^{-26}
Hg_2Cl_2	1.1×10^{-18}
Hg_2Br_2	1.3×10^{-22}
Hg_2I_2	4.5×10^{-29}
Hg_2CO_3	9×10^{-15}
Hg_2SO_4	7.4×10^{-7}
Hg_2S	1.0×10^{-47}
Hg_2CrO_4	2×10^{-9}
HgS	1.6×10^{-54}
nickel	
$Ni(OH)_2$	1.6×10^{-16}
$NiCO_3$	1.4×10^{-7}
NiS(α)	4×10^{-20}
NiS(β)	1.3×10^{-25}
potassium	
$KClO_4$	1.05×10^{-2}
K_2PtCl_6	7.48×10^{-6}
$KHC_4H_4O_6$	3×10^{-4}
silver	
$\frac{1}{2}Ag_2O(Ag^+ + OH^-)$	2×10^{-8}
AgCl	1.6×10^{-10}
AgBr	5.0×10^{-13}
AgI	1.5×10^{-16}
AgCN	1.2×10^{-16}
AgSCN	1.0×10^{-12}
Ag_2S	1.6×10^{-49}
Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	9.0×10^{-12}
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.2×10^{-5}
Ag_3PO_4	1.8×10^{-18}
strontium	

Substance	K_{sp} at 25 °C
$Sr(OH)_2 \cdot 8H_2O$	3.2×10^{-4}
$SrCO_3$	7×10^{-10}
$SrCrO_4$	3.6×10^{-5}
$SrSO_4$	3.2×10^{-7}
$SrC_2O_4 \cdot H_2O$	4×10^{-7}
thallium	
TlCl	1.7×10^{-4}
TlSCN	1.6×10^{-4}
Tl_2S	6×10^{-22}
$Tl(OH)_3$	6.3×10^{-46}
tin	
$Sn(OH)_2$	3×10^{-27}
SnS	1×10^{-26}
$Sn(OH)_4$	1.0×10^{-57}
zinc	
$ZnCO_3$	2×10^{-10}

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4.8: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 4.8.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 4.8.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $\mathbf{Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)}$. *The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the* $Fe(SCN)^{2+}$. *(credit: modification of work by Mark Ott).*

Three capped test tubes held vertically in clamps are shown in pictures labeled, "a," "b," and "c." The test tube in picture a is half filled with a clear, orange liquid. The test tube in picture b is half filled with a dark, burgundy liquid. The test tube in picture c is half filled with a slightly cloudy, orange liquid.

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}} \tag{4.8.1}$$

$$K_c = 50.0 \text{ at } 400°C \tag{4.8.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{4.8.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO\,(g) + O_2\,(g) \ \mhchemrightleftharpoons 2\,NO_2\,(g) \tag{4.8.4}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2\,(g) + O_2\,(g) \ \mhchemrightleftharpoons 2\,NO\,(g) \tag{4.8.5}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

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.

$$\mathrm{H_2\,(g) + I_2\,(g) \mhchemrightleftharpoons 2\,HI\,(g)} \quad (4.8.6)$$
$$\Delta H = -9.4\ \mathrm{kJ\ (exothermic)}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2\,(g) + I_2\,(g) \mhchemrightleftharpoons 2\,HI\,(g) + heat} \quad (4.8.7)$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of $\mathrm{H_2}$ and $\mathrm{I_2}$ and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ in this reaction

$$\mathrm{N_2O_4\,(g) \mhchemrightleftharpoons 2\,NO_2\,(g)} \quad \Delta H = 57.20\ \mathrm{kJ} \quad (4.8.8)$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4\,(g) \mhchemrightleftharpoons 2\,NO_2\,(g)} \quad (4.8.9)$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathrm{NO_2}$ molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless $\mathrm{N_2O_4}$ increases, and the concentration of brown $\mathrm{NO_2}$ decreases, causing the brown color to fade.

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \mhchemrightleftharpoons 2\,NH_3\,(g)} \quad (4.8.10)$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)\ \mhchemrightleftharpoons 2\,NH_3\,(g)}$$

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen ($\mathbf{N_2}$) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)\ \mhchemrightleftharpoons 2\,NH_3\,(g)} \tag{4.8.11}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g)\ \rightarrow 2\,NH_3\,(g)}\quad \Delta H = -92.2\ \mathrm{kJ} \tag{4.8.12}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure **4.8.2**).

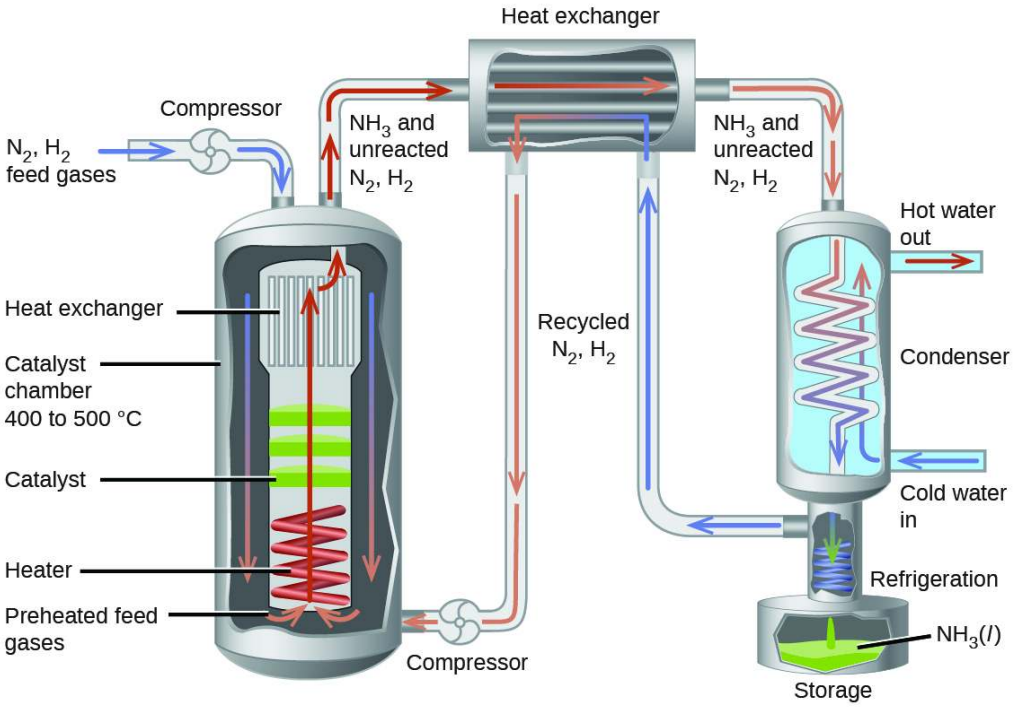


Figure **4.8.2**: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Table **4.8.1**: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle
when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium
concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress
change to a reaction's conditions that may cause a shift in the equilibrium

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CHAPTER OVERVIEW

5: Acids and Bases

5.1: Acids and Bases - A Brief Review
5.2: Brønsted–Lowry Acids and Bases
5.3: Lewis Acids and Bases
5.4: The Autoionization of Water
5.5: The pH Scale
5.6: Strong Acids and Bases
5.7: Weak Acids
5.8: Ionization Constants of Weak Acids
5.9: Weak Bases
5.10: Ionization Constants of Weak Bases
5.11: Relationship Between Ka and Kb
5.12: Acid-Base Properties of Salt Solutions
5.13: The Common-Ion Effect
5.14: Buffered Solutions
5.15: Acid-Base Titrations

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5.1: Acids and Bases - A Brief Review

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

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 5.1.1).

Table 5.1.1: 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.

The Arrhenius Definition of 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. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, hydrochloric acid (HCl) dissociates into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

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.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definition can **only** describe acids and bases in an aqueous environment.

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 alter in the chapter and 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.

Contributors and Attributions

- Anonymous

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5.2: Brønsted–Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Previously, we defined acids and bases as Arrhenius did: An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. 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). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{5.2.1}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{5.2.2}$$

$$HF \mhchemrightleftharpoons H^+ + F^- \tag{5.2.3}$$

$$H_2SO_4 \mhchemrightleftharpoons H^+ + HSO_4^- \tag{5.2.4}$$

$$H_2O \mhchemrightleftharpoons H^+ + OH^- \tag{5.2.5}$$

$$HSO_4^- \mhchemrightleftharpoons H^+ + SO_4^{2-} \tag{5.2.6}$$

$$NH_4^+ \mhchemrightleftharpoons H^+ + NH_3 \tag{5.2.7}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{5.2.8}$$

$$\mathrm{OH^- + H^+ \mhchemrightleftharpoons H_2O} \tag{5.2.9}$$

$$\mathrm{H_2O + H^+ \mhchemrightleftharpoons H_3O^+} \tag{5.2.10}$$

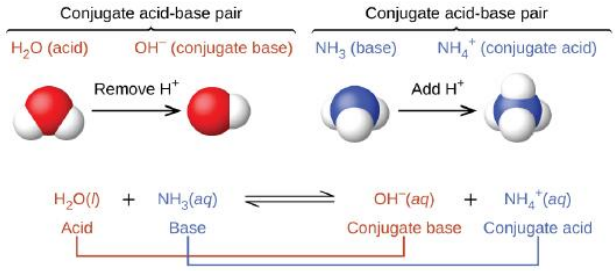
$$\mathrm{NH_3 + H^+ \mhchemrightleftharpoons NH_4^+} \tag{5.2.11}$$

$$\mathrm{S^{2-} + H^+ \mhchemrightleftharpoons HS^-} \tag{5.2.12}$$

$$\mathrm{CO_3^{2-} + H^+ \mhchemrightleftharpoons HCO_3^-} \tag{5.2.13}$$

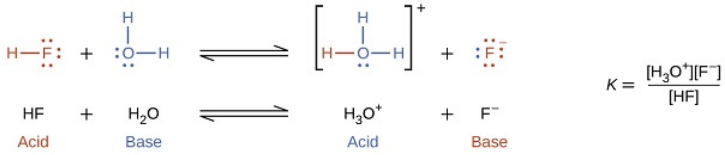
\[\ce{F^- +H^+ \rightleftharpoons HF} \label{16.2.3g} \]

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, $\mathrm{OH^-}$, and the conjugate acid of ammonia, $\mathrm{NH_4^+}$:



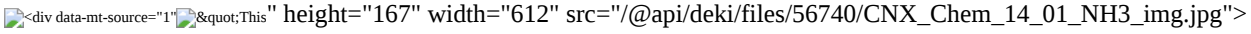
A conjugate acid base pair if when we remove a H plus from the acid to get the conjugate base. Another conjugate acid base pair is when we add H plus to a base to get a conjugate acid. In a reaction: the acid and base are the reactants and the products are the conjugate base and conjugate acid.

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:

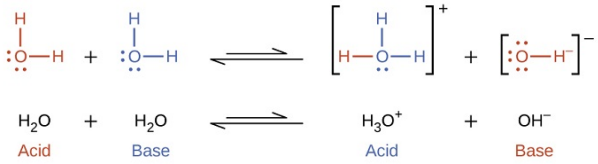


In this reaction HF is treated as the acid and water is treated as the base. The products as H3O plus and F minus. H3O plus is the acid and F minus is the base.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



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:



Here we have 2 water molecules reacting together. One water molecule is an acid while the second water molecule acts as a base. For the products, we get H3O plus and OH minus. H3O plus is the acid and OH minus is the base.

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):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HO^-_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{5.2.14}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.



A Video Discussing Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs [youtu.be]

Example 5.2.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^{2+} = [OH^-]^{2+} = 1.0 \times 10^{-14}$$

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 5.2.1

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 determined by the autoionization reaction but it does shift the relative concentrations of $[OH^-]$ and $[H_3O^+]$. Example 16.2.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw) [youtu.be]

Example 5.2.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

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 5.2.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)}} \tag{5.2.15}$$

$$\mathrm{HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)}} \tag{5.2.16}$$

✔ Example 5.2.3: 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. $HSO^-_{3(aq)} + OH^-_{(aq)} \rightleftharpoons SO^{2-}_{3(aq)} + H_2O_{(l)}$
b. $HSO^-_{3(aq)} + HI_{(aq)} \rightleftharpoons H_2SO_{3(aq)} + I^-_{(aq)}$

? Example 5.2.4

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. $H_2PO^-_{4(aq)} + HBr_{(aq)} \rightleftharpoons H_3PO_{4(aq)} + Br^-_{(aq)}$
b. $H_2PO^-_{4(aq)} + OH^-_{(aq)} \rightleftharpoons HPO^{2-}_{4(aq)} + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes autoionization:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [\mathrm{H_2O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25°\mathrm{C}$$

Key Equations

- $$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization

reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

Contributors and Attributions

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5.3: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- 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.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

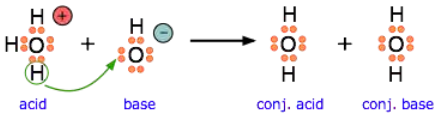
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of 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. 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.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

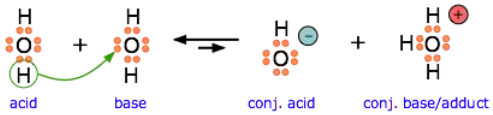
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



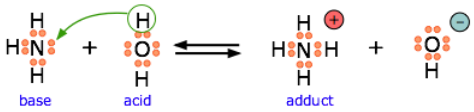
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully 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.

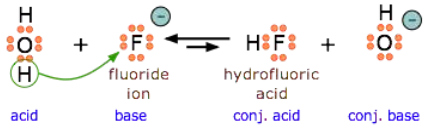
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product 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.



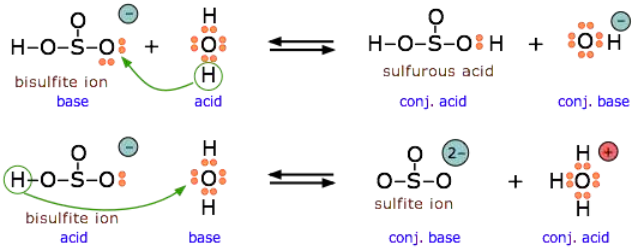
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



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.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$\mathbf{BF_3 + NH_3 \rightarrow F_3B{-}NH_3} \tag{5.3.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

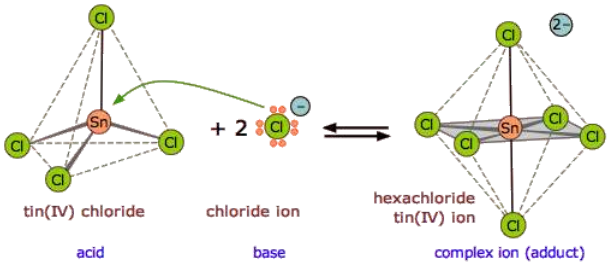


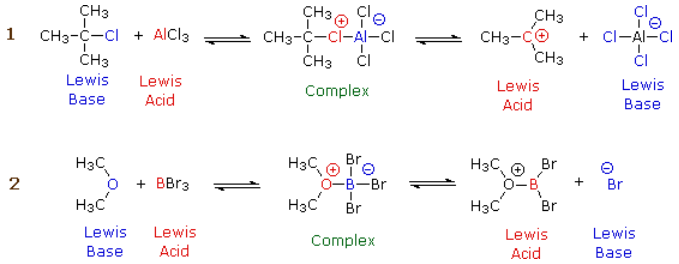
Figure **5.3.1**: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

? Exercise 5.3.1

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. $Cd(CN)_2 + 2\,CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table 5.3.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 5.3.1 indicates:

Table 5.3.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\,CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\,C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\,HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\,HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\,H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

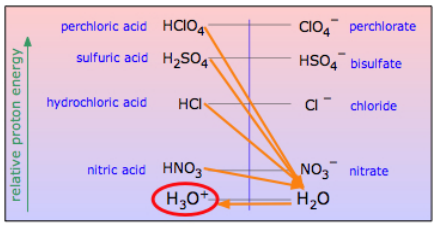


Figure **5.3.2**: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

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5.4: The Autoionization of Water

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

As you learned previously acids and bases can be defined in several different ways (Table 5.4.1). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can donate a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can accept a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve two conjugate acid–base pairs and the transfer of a proton from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, focuses on accepting or donating pairs of electrons rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table 5.4.1: Definitions of Acids and Bases

Definition	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in aqueous solution, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{\text{acid}}{HCl_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightarrow \underset{\text{acid}}{H_3O^+_{(aq)}} + \underset{\text{base}}{Cl^-_{(aq)}} \tag{5.4.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 5.4.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{5.4.2}$$

In Equation 5.4.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

Water can also act as an acid, as shown in Equation 5.4.3. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{\text{acid}}{H_2O_{(l)}} + \underset{\text{base}}{NH_{3(aq)}} \rightleftharpoons \underset{\text{acid}}{NH^+_{4(aq)}} + \underset{\text{base}}{OH^-_{(aq)}} \tag{5.4.3}$$

Water is thus termed amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 5.4.3 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{5.4.4}$$

The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{5.4.5}$$

where a is the activity of a species. Because water is the solvent, and 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 activity of each solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that Ka = $K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation Ka = $K_{eq}(a_{H_2O})$. Because a_{H_2O} = 1 for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{5.4.6}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25 °C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{5.4.7}$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25 °C into this expression

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{5.4.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ *at room temperature*, and

$$K_w = 1.01 \times 10^{-14} = [H_3O^+][OH^-] \tag{5.4.9}$$

.

Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0 °C to 4.99×10^{-13} at 100 °C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+

and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw): [youtu.be]

The Relationship among pH, pOH, and pK_w

The pH scale is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[H^+] \tag{5.4.10}$$

$$[H^+] = 10^{-pH} \tag{5.4.11}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}\ M$), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -\log_{10}[OH^-] \tag{5.4.12}$$

$$[OH^-] = 10^{-pOH} \tag{5.4.13}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log\ K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25 °C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25 °C by taking the negative logarithm of both sides of Equation ???:

$$-\log_{10} K_w = pK_w \tag{5.4.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{5.4.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{5.4.16}$$

$$= pH + pOH \tag{5.4.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25 °C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure 5.4.1 over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

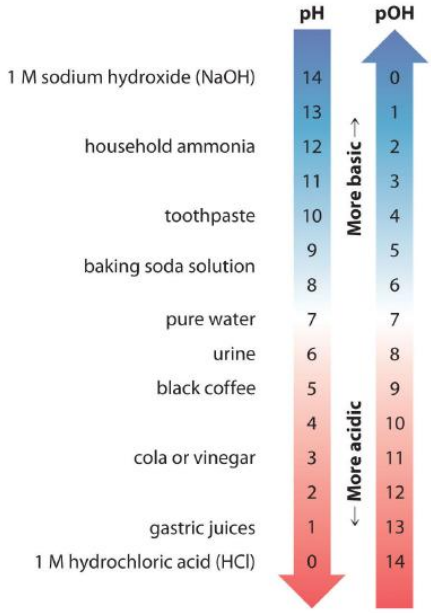


Figure 5.4.1: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

Zero is the most acidic and fourteen is the most basic on the pH scale. Zero is the most basic and fourteen is the most acidic on the pOH scale.

> *For any neutral solution, pH + pOH = 14.00 (at 25 °C) with pH=pOH=7.*



A Video Introduction to pH: Introduction to pH [youtu.be]

Example 5.4.1

The K_w for water at 100 °C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100 °C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pK_w by taking the negative logarithm of K_w.

B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 5.4.9 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A

Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B

Equation ??? shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (x)(x) = x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\begin{aligned} pH = pOH &= -\log(7.06 \times 10^{-7}) \\ &= 6.15 \text{ (to two decimal places)} \end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 5.4.17, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 5.4.17 directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$\begin{aligned} pK_w &= pH + pOH \\ &= y + y \\ &= 2y \\ y &= \frac{pK_w}{2} \\ &= \frac{12.302}{2} \\ &= 6.15 = pH = pOH \end{aligned}$$

? Exercise 5.4.1

Humans maintain an internal temperature of about 37 °C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37 °C. Report pH and pOH values to two decimal places.

Answer

- $pK_w = 13.45$
- $pH = pOH = 6.73$

Summary

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (Kw) and is defined as $K_w = [H_3O^+][OH^-]$. At 25 °C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$.

- For any neutral solution, $pH + pOH = 14.00$ (at 25 °C) and $pH = 1/2pK_w$.
- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log 10[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^+]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

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5.5: The pH Scale

Learning Objectives

- To define the pH scale as a measure of acidity of a solution

Because of its *amphoteric* nature (i.e., acts as both an acid or a base), water does not always remain as H_2O molecules. In fact, two water molecules react to form hydronium and hydroxide ions:

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq) \tag{5.5.1}$$

This is also called the self-ionization of water. The concentration of H_3O^+ and OH^- are equal in pure water because of the 1:1 stoichiometric ratio of Equation 1. The molarity of H_3O^+ and OH^- in water are also both $1.0 \times 10^{-7}\ M$ at 25° C. Therefore, a constant of water (K_w) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10^{-14}.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{5.5.2}$$

This equations also applies to all aqueous solutions. However, K_w does change at different temperatures, which affects the pH range discussed below.

> *H^+ and H_3O^+ is often used interchangeably to represent the hydrated proton, commonly call the hydronium ion.*

The equation for water equilibrium is:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{5.5.3}$$

- If an acid (H^+) is added to the water, the equilibrium shifts to the left and the OH^- ion concentration decreases
- If base (OH^-) is added to water, the equilibrium shifts to left and the H^+ concentration decreases.

pH and pOH

The constant of water determines the range of the pH scale. To understand what the pK_w is, it is important to understand first what the "p" means in pOH, and pH. The Danish biochemist Søren Sørenson proposed the term pH to refer to the "potential of hydrogen ion." He defined the "p" as the negative of the logarithm, -log, of [H^+]. Therefore the pH is the negative logarithm of the molarity of H. The pOH is the negative logarithm of the molarity of OH^- and the pK_w is the negative logarithm of the constant of water. These definitions give the following equations:

$$pH = -\log[H^+] \tag{5.5.4}$$

$$pOH = -\log[OH^-] \tag{5.5.5}$$

$$pK_w = -\log[K_w] \tag{5.5.6}$$

At room temperature (25 °C),

$$K_w = 1.0 \times 10^{-14} \tag{5.5.7}$$

So

$$pK_w = -\log[1.0 \times 10^{-14}] \tag{5.5.8}$$

Using the properties of logarithms, Equation 5.5.8 can be rewritten as

$$10^{-pK_w} = 10^{-14}. \tag{5.5.9}$$

By substituting, we see that pK_w is 14. The equation also shows that each increasing unit on the scale decreases by the factor of ten on the concentration of H^+. For example, a pH of 1 has a molarity ten times more concentrated than a solution of pH 2.

Since

$$pK_w = 14 \tag{5.5.10}$$

$$pK_w = pH + pOH = 14 \tag{5.5.11}$$

Definitions

- A solution with more OH^- ions than H^+ ion is **basic;** for aqueous solutions at 25°C that corresponds to pH > 7.
- A solution with more H^+ ions than OH^- ions is **acidic;** for aqueous solutions at 25°C that corresponds to pH < 7.
- A solution with that same concentration of H^+ ions than OH^- ions is **neutral;** for aqueous solutions at 25°C that corresponds to pH = 7.

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:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.9 \times 10^{-7}) = 6.31 \tag{5.5.12}$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.9 \times 10^{-7}) = 6.31 \tag{5.5.13}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 5.5.1).

> *The pH scale is logarithmic, meaning that an increase or decrease of an integer value changes the concentration by a tenfold. For example, a pH of 3 is ten times more acidic than a pH of 4. Likewise, a pH of 3 is one hundred times more acidic than a pH of 5. Similarly a pH of 11 is ten times more basic than a pH of 10.*

Figure 5.5.1 depicts the pH scale with common solutions and where they are on the scale.

$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^{1}	10^{-15}	–1	15	
10^{0} or 1	10^{-14}	0	14	1 M HCl
10^{-1}	10^{-13}	1	13	
10^{-2}	10^{-12}	2	12	gastric juice, lime juice, 1 M CH_3CO_2H (vinegar)
10^{-3}	10^{-11}	3	11	stomach acid
10^{-4}	10^{-10}	4	10	wine, orange juice
10^{-5}	10^{-9}	5	9	coffee
10^{-6}	10^{-8}	6	8	rain water
10^{-7}	10^{-7}	7	7	pure water
10^{-8}	10^{-6}	8	6	blood, ocean water
10^{-9}	10^{-5}	9	5	baking soda
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	Milk of Magnesia
10^{-12}	10^{-2}	12	2	household ammonia, NH_3
10^{-13}	10^{-1}	13	1	bleach
10^{-14}	10^{0} or 1	14	0	1 M NaOH
10^{-15}	10^{1}	15	–1	

acidic

neutral

basic

Figure 5.5.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart. Image used with permisison (CC -BY; OpenStax)

The pH scale does not have upper nor lower bounds!

It is common that the pH scale is argued to range from 0-14 or perhaps 1-14, but neither is correct. The pH range does not have an upper nor lower bound, since as defined above, the pH is an indication of concentration of H^+. For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Hence a range of 0 to 14 provides sensible (but not absolute) "bookends" for the scale. One can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar.

Example 5.5.1

If the concentration of $NaOH$ in a solution is $2.5 \times 10^{-4}\ M$, what is the concentration of H_3O^+?

Solution

Because

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

to find the concentration of H_3O^+, solve for the $[H_3O^+]$.

$$\frac{1.0 \times 10^{-14}}{[OH^-]} = [H_3O^+]$$

$$\frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}} = [H_3O^+] = 4.0 \times 10^{-11}\ M$$

Example 5.5.2

a. Find the pH of a solution of 0.002 M of HCl.
b. Find the pH of a solution of 0.00005 M NaOH.

Solution

a. The equation for pH is -log [H+]

$$[H^+] = 2.0 \times 10^{-3}\ M$$

$$pH = -\log[2.0 \times 10^{-3}] = 2.70$$

b. The equation for pOH is -log [OH^-]

$$[OH^-] = 5.0 \times 10^{-5}\ M$$

$$pOH = -\log[5.0 \times 10^{-5}] = 4.30$$

$$pK_w = pH + pOH$$

and

$$pH = pK_w - pOH$$

then

$$pH = 14 - 4.30 = 9.70$$

Example 5.5.3: Soil

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

Solution

$$pH = -\log[H^+]$$

$$7.84 = -\log[H^+]$$

$$[H^+] = 1.45 \times 10^{-8} M$$

Hint: Place -7.84 in your calculator and take the antilog (often inverse log or 10^x) = 1.45 x 10^{-8}M



A Video Introduction to pH: Introduction to pH [youtu.be]

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00.

References

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5.6: Strong Acids and Bases

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{5.6.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{5.6.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 5.6.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 5.6.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{5.6.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 5.6.1.

Table 5.6.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
*The number in parentheses indicates the ionization step referred to for a polyprotic acid.						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{5.6.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{5.6.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 5.6.2.

Table 5.6.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0^*	0.00
*As in Table 5.6.1.						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{5.6.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{5.6.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{5.6.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{5.6.9}$$

If we add Equations 5.6.6 and 5.6.7, we obtain the following:

add Equations 5.6.6 and 5.6.7, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,[\cancel{CN^-}]\,/\,[\cancel{HCN}]$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,[\cancel{HCN}]\,/\,[\cancel{CN^-}]$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_a K_b = K_w \tag{5.6.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{5.6.11}$$

$$K_a = 10^{-pK_a} \tag{5.6.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{5.6.13}$$

$$K_b = 10^{-pK_b} \tag{5.6.14}$$

Similarly, Equation 5.6.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{5.6.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{5.6.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 5.6.1 and 5.6.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

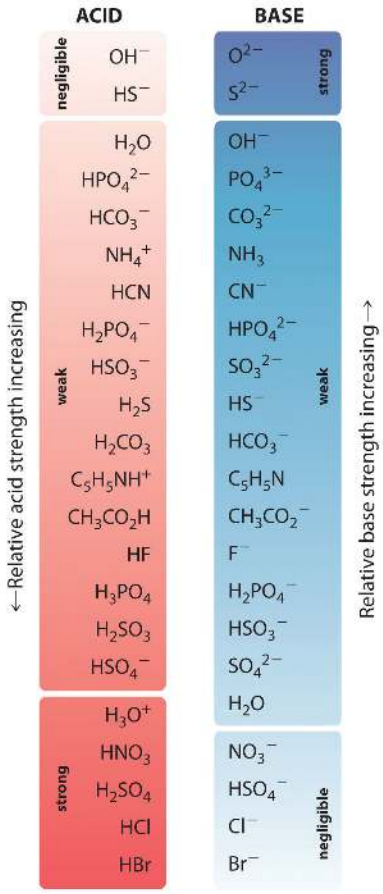


Figure 5.6.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 5.6.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 5.6.2 are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{5.6.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO^-_{2\,(aq)}}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 5.6.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 5.6.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations 5.6.15 and 5.6.16. Use the relationships pK = −log K and K = 10^{-pK} (Equations 5.6.11 and 5.6.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 5.6.16: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 5.6.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

? Exercise 5.6.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 5.6.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 5.6.1 were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 5.6.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{5.6.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{5.6.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{5.6.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO^{2-}_{4(aq)} + H_2O_{(aq)} \rightleftharpoons HSO^-_{4(aq)} + OH^-_{(aq)}$$

$$HSO^-_{4(aq)} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH^-_{(aq)} \tag{5.6.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by $pK_a + pK_b$ = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table 5.6.1, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation 5.6.21 lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

✔ Example 5.6.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH^+_{4(aq)} + PO^{3-}_{4(aq)} \rightleftharpoons NH_{3(aq)} + HPO^{2-}_{4(aq)}$
- $CH_3CH_2CO_2H_{(aq)} + CN^-_{(aq)} \rightleftharpoons CH_3CH_2CO^-_{2(aq)} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables 5.6.1and5.6.2 and Figure 5.6.2 to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables 5.6.1 and 5.6.2, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH_{4(aq)}^+} + \underset{\text{stronger base}}{PO_{4(aq)}^{3-}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO_{4(aq)}^{2-}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table 5.6.1, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table 5.6.1, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN_{(aq)}^-} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO_{2(aq)}^-} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

? Exercise 5.6.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

a. $H_2O_{(l)} + HS_{(aq)}^- \rightleftharpoons OH_{(aq)}^- + H_2S_{(aq)}$
b. $HCO_{2(aq)}^- + HSO_{4(aq)}^- \rightleftharpoons HCO_2H_{(aq)} + SO_{4(aq)}^{2-}$

Answer a

left

Answer b

left



A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases.

For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C}$$

Contributors and Attributions

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5.7: Weak Acids

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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

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 5.7.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 5.7.1: 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

we write the equation for the ionization constant as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

The larger the K_a of an acid, the larger the concentration of H_3O^+ and 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: $CH_3CO_2H < HNO_2 < HSO_4^-$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$
$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \qquad K_a = 4.6 \times 10^{-4}$$
$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

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:

$$\%\ \text{ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{5.7.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 5.7.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 5.7.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 5.7.1

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:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

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 5.7.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, **B**:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_b = \frac{[HB+][OH-]}{[B]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 1.8 \times 10^{-5}$$

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, $\mathrm{HA - A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

with $K_a = \frac{[H3O+][A-]}{[HA]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq)$$

with $K_b = \frac{[HA][OH]}{[A-]}$.

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:

$$K_a \times K_b = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($\mathrm{CH_3COO^-}$), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w$$

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 **5.7.2**).

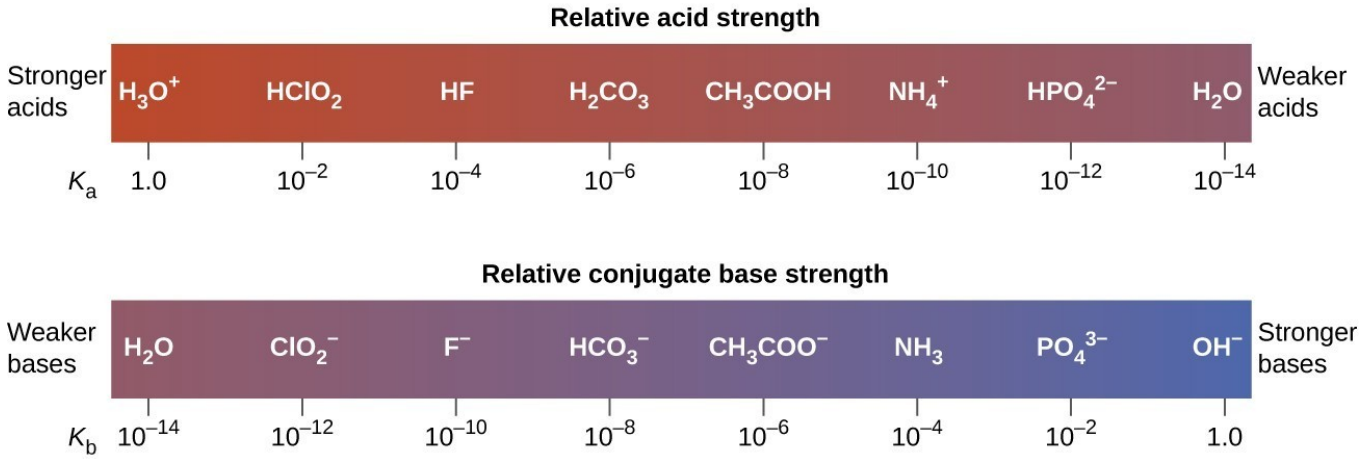


Figure **5.7.2**: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure **5.7.3** 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 **5.7.3** 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 **5.7.3** 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 **5.7.3** 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.

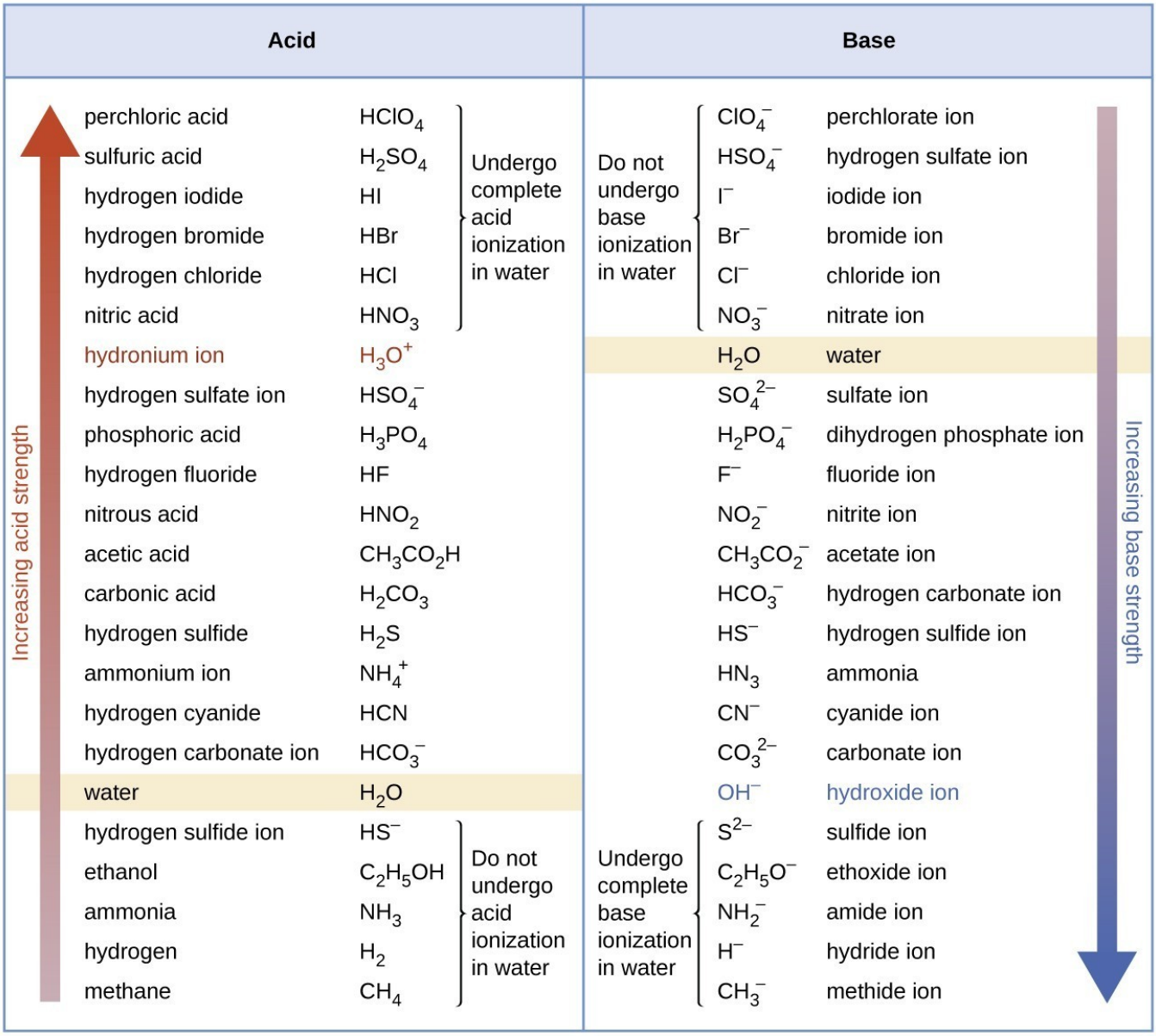


Figure **5.7.3**: The chart shows the relative strengths of conjugate acid-base pairs.

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 **5.7.3**. 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 5.7.2: 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 5.7.2

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 $NH_4^+ = 5.6 \times 10^{-10}$).

The Ionization of Weak Acids and Weak Bases

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 5.7.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} = 1.8 \times 10^{-5}$$



Figure 5.7.4: 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)

This image shows two bottles containing clear colorless solutions. Each bottle contains a single p H indicator strip. The strip in the bottle on the left is red, and a similar red strip is placed on a filter paper circle in front of the bottle on surface on which the bottles are resting. Similarly, the second bottle on the right contains and orange strip and an orange strip is placed in front of it on a filter paper circle. Between the two bottles is a pack of p Hydrion papers with a p H color scale on its cover.

Table 5.7.1: 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}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 5.7.1 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 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]}$$



Figure 5.7.5: 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 5.7.2 and Table E2.

Table 5.7.2: 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 5.7.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 M and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by “HomeSpot HQ”/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

? Exercise 5.7.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29\ M$; and $[SO_4^{2-}] = 0.13\ M$.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

✓ Example 5.7.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0 × 10^{-3} *M*, and $[OH^-]$ = 2.5 × 10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

so

$$K_b = \frac{[C8H10N4O2H+][OH-]}{[C8H10N4O2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

? Exercise 5.7.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0.042 M and
- $[HPO_4^{2-}]$=0.341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

✓ Example 5.7.5: Determination of K_a or K_b from pH

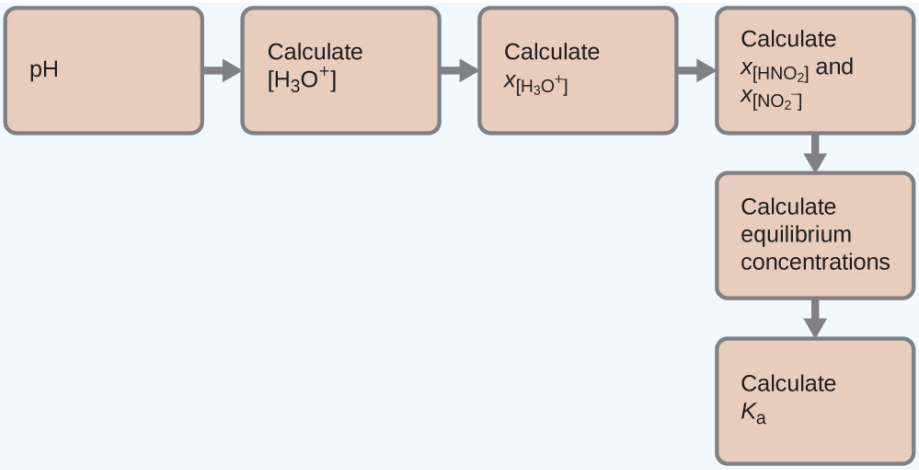
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

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. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	x	x
Equilibrium concentration (*M*)	$[HNO_2]_i + (-x) = 0.0516 + (-x)$		$[H_3O]^+ + x[NO_2]^- + x \sim 0 + x$	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 + H_2O ⇌ H_3O^+ + NO_2^-			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H3O+][NO2-]}{[HNO2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 5.7.5

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 5.7.6: 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?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \quad K_a = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O ⇌	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.534 + (-x)$	$0 + x = x$	$0 + x = x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_a = 1.8 \times 10^{-4} = \frac{[H3O+][HCO2-]}{[HCO2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$
$$= 9.6 \times 10^{-5}$$
$$x = \sqrt{9.6 \times 10^{-5}}$$
$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$
$$= 1.8 \times 10^{-2} (1.8$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[H_3O^+] = \ 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$
$$= 9.8 \times 10^{-3}\ M$$

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 5.7.6: 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 $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Answer

percent ionization = 1.3%

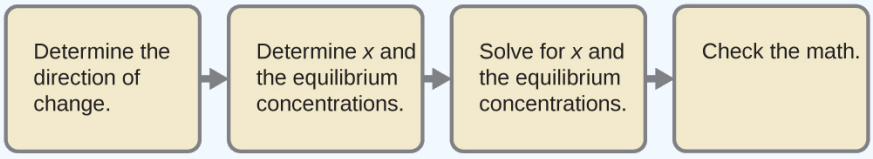
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 5.7.7: 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 5.7.6. 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*)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([OH^-] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 5.7.7

a. Show that the calculation in Step 2 of this example gives an x of 4.3×10^{-3} and the calculation in Step 3 shows $K_b = 6.3 \times 10^{-5}$.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[NH4+]}{[NH3]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that x is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

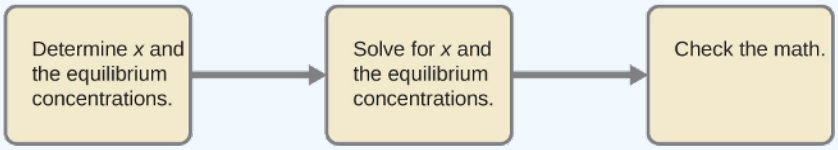
Example 5.7.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌	H_3O^+	+ SO_4^{2-}
Initial concentration (*M*)	0.50	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$	$0 + x = x$	$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2-}]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that x is small and approximate $(0.50 - x)$ as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

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:

$$\begin{aligned}[\mathrm{H_3O^+}] = \ & 0 + x = 0 + 7.2 \times 10^{-2}\ M \\ & = 7.2 \times 10^{-2}\ M\end{aligned}$$

The pH of this solution is:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 5.7.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.

b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\mathrm{C_8H_{10}N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) + \mathrm{OH^-}(aq) \quad K_\mathrm{b} = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert [OH⁻] to [$\mathrm{H_3O^+}$] or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as **HCl**, **HBr**, and **HI**, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find **HCl**, **HBr**, and **HI** differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order **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, $\mathbf{NH_2^-}$, are such strong bases that they react completely with water:

$$\mathrm{O^{2-}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{OH^-}(aq) + \mathrm{OH^-}(aq)$$

$$\mathrm{NH_2^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{OH^-}(aq)$$

Thus, O^{2-} and $\mathbf{NH_2^-}$ 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 5.7.6).

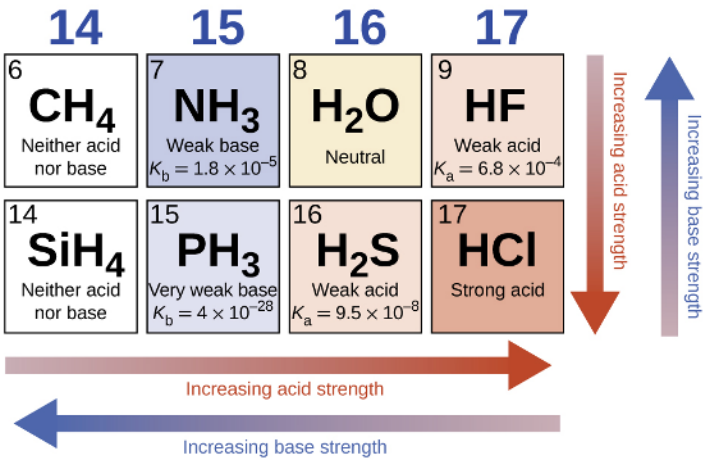
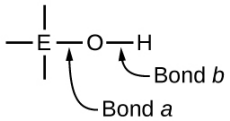


Figure 5.7.6: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

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:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure **5.7.7**).

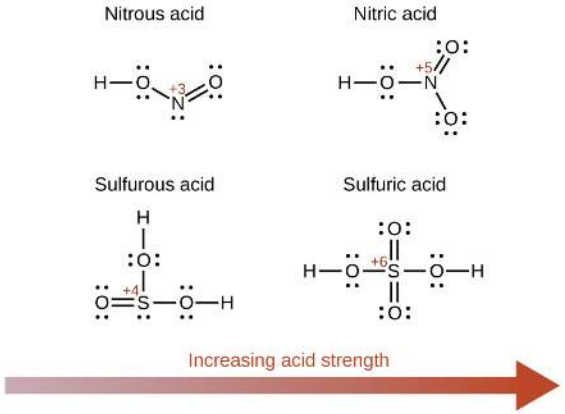


Figure **5.7.7**: As the oxidation number of the central atom E increases, the acidity also increases.

A diagram is shown that includes four structural formulas for acids. A red, right pointing arrow is placed beneath the structures which is labeled “Increasing acid strength.” At the top left, the structure of Nitrous acid is provided. It includes an H atom to which an O atom with two unshared electron pairs is connected with a single bond to the right. A single bond extends to the right and slightly below to a N atom with one unshared electron pair. A double bond extends up and to the right from this N atom to an O atom which has two unshared electron pairs. To the upper right is a structure for Nitric acid. This structure differs from the previous structure in that the N atom is directly to the right of the first O atom and a second O atom with three unshared electron pairs is connected with a single bond below and to the right of the N atom which has no unshared electron pairs. At the lower left, an O atom with two unshared electron pairs is double bonded to its right to an S atom with a single unshared electron pair. An O atom with two unshared electron pairs is bonded above and an H atom is single bonded to this O atom. To the right of the S atom is a single bond to another O atom with two unshared electron pairs to which an H atom is single bonded. This structure is labeled “Sulfurous acid.” A similar structure which is labeled “Sulfuric acid” is placed in the lower right region of the figure. This structure differs in that an H atom is single bonded to the left of the first O atom, leaving it with two unshared electron pairs and a fourth O atom with two unshared electron pairs is double bonded beneath the S atom, leaving it with no unshared electron pairs.

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 $\mathbf{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathbf{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathbf{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathbf{[Al(H_2O)_3(OH)_3](\mathit{aq}) + OH^-(\mathit{aq}) \rightleftharpoons H_2O(\mathit{l}) + [Al(H_2O)_2(OH)_4]^-(\mathit{aq})}$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\mathbf{Al(H_2O)_3(OH)_3}$ 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 $\mathbf{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$\mathbf{3\,H_3O^+(\mathit{aq}) + Al(H_2O)_3(OH)_3(\mathit{aq}) \rightleftharpoons Al(H_2O)_6^{3+}(\mathit{aq}) + 3\,H_2O(\mathit{l})}$$

In this case, protons are transferred from hydronium ions in solution to $\mathbf{Al(H_2O)_3(OH)_3}$, 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

- $K_a = \frac{[H3O+][A-]}{[HA]}$
- $K_b = \frac{[HB+][OH-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100$

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

leveling effect of water
any acid stronger than 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

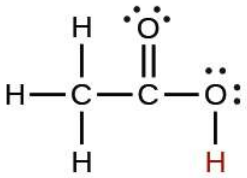
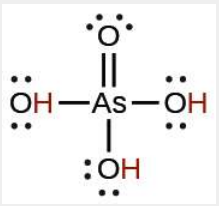
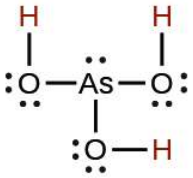
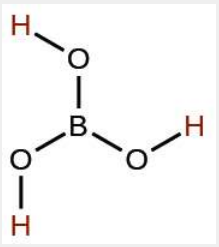
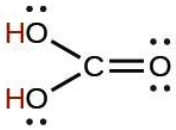
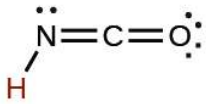
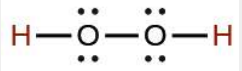
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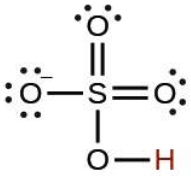
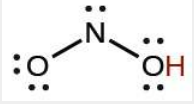
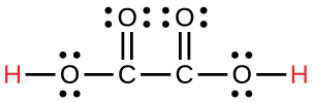
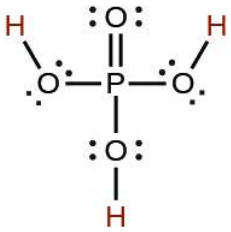
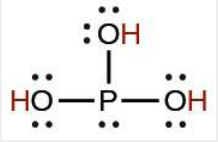
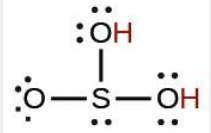
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5.8: Ionization Constants of Weak Acids

Ionization Constants of Weak Acids

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Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
acetic	$CH_3CO_2\mathbf{H}$	1.8×10^{-5}	
arsenic	$\mathbf{H_3}AsO_4$	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	5.1×10^{-12}	
arsenous	$\mathbf{H_3}AsO_3$	5.1×10^{-10}	
boric	$\mathbf{H_3}BO_3$	5.4×10^{-10}	
carbonic	$\mathbf{H_2}CO_3$	4.3×10^{-7}	
	HCO_3^-	4.7×10^{-11}	
cyanic	**H**CNO	2×10^{-4}	
formic	$HCO_2\mathbf{H}$	1.8×10^{-4}	
hydrazoic	$\mathbf{H}N_3$	2.5×10^{-5}	
hydrocyanic	**H**CN	4.9×10^{-10}	
hydrofluoric	**H**F	3.5×10^{-4}	
hydrogen peroxide	$\mathbf{H_2}O_2$	2.4×10^{-12}	
hydrogen selenide	$\mathbf{H_2}Se$	1.29×10^{-4}	
	$\mathbf{H}Se^-$	1×10^{-12}	

Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	HBrO	2.8×10^{-9}	
hypochlorous	HClO	2.9×10^{-8}	
nitrous	HNO_2	4.6×10^{-4}	
oxalic	$H_2C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	
phosphoric	H_3PO_4	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	H_3PO_3	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	H_2SO_3	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

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5.9: Weak Bases

The pH of a solution of a weak base can be calculated in a way which is very similar to that used for a weak acid. Instead of an acid constant K_a, a base constant K_b must be used. If a weak base B accepts protons from water according to the equation

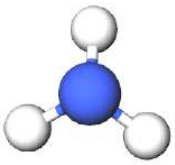
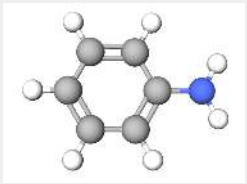
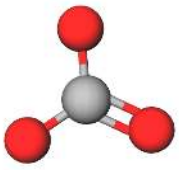
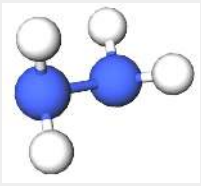
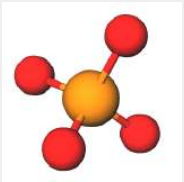
$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH^+} + \mathrm{OH^-} \tag{5.9.1}$$

then the base constant is defined by the expression

$$K_b = \frac{\mathrm{BH^+}\ \mathrm{OH^-}}{\mathrm{B}} \tag{5.9.2}$$

A list of K_b values for selected bases arranged in order of strength is given in the table below. This table is part of our larger collection of acid-base resources.

Table **5.9.1**: The Base Constants for Some Bases at 25°C. Taken from Hogfelt, E. Perrin, D. D. Stability Constants of Metal Ion Complexes, 1st ed. Oxford; New Pergamon, 1979-1982. International Union of Pure and Applied Chemistry, Commission on Equilibrium. ISBN: 0080209580

Base	Formula and Ionization Equation	K_b	Molecular Shape
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.77×10^{-5}	
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	3.9×10^{-10}	
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	2.1×10^{-4}	
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_1 = 1.2 \times 10^{-6}$ $K_2 = 1.3 \times 10^{-15}$	
Hydride ion	$H^- + H_2O \rightarrow H_2 + OH^-$	1.0	
Phosphate ion	$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$	5.9×10^{-3}	
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.6×10^{-9}	

To find the pH we follow the same general procedure as in the case of a weak acid. If the stoichiometric concentration of the base is indicated by c_b, the result is entirely analogous to equation 4 in the section on the pH of weak acids; namely,

$$K_b = \frac{[\mathrm{OH^-}]^2}{c_b - [\mathrm{OH^-}]} \tag{5.9.3}$$

Under most circumstances we can make the approximation

$$c_b - [OH^-] \approx c_b$$

in which case Equation 5.9.3 reduces to the approximation

$$[OH^-] \approx \sqrt{K_b c_b} \tag{5.9.4}$$

which is identical to the expression obtained in the acid case (approximation shown in equation 6 in the section on the pH of weak acids) except that OH^- replaces H_3O^+ and *b* replaces *a*. Once we have found the hydroxide-ion concentration from this approximation, we can then easily find the pOH, and from it the pH.

Example 5.9.1: pH using K_b

Using the value for K_b listed in the table, find the pH of 0.100 *M* NH_3.

Solution

It is not a bad idea to guess an approximate pH before embarking on the calculation. Since we have a dilute solution of a weak base, we expect the solution to be only mildly basic. A pH of 13 or 14 would be too basic, while a pH of 8 or 9 is too close to neutral. A pH of 10 or 11 seems reasonable. Using Equation 5.9.4 we have

$$\begin{aligned}[\text{OH}^-] &= \sqrt{K_b c_b} \\ &= \sqrt{1.8 \times 10^{-5}\ \text{mol L}^{-1} \times 0.100\ \text{mol L}^{-1}} \\ &= \sqrt{1.8 \times 10^{-6}\ \text{mol}^2\ \text{L}^{-2}} \\ &= 1.34 \times 10^{-3}\ \text{mol L}^{-1}\end{aligned}$$

Checking the accuracy of the approximation, we find

$$\frac{[\text{OH}^-]}{c_b} = \frac{1.34 \times 10^{-3}}{0.1} \approx 1\ \text{percent}$$

The approximation is valid, and we thus proceed to find the pOH.

$$\text{pOH} = -\log\frac{[\text{OH}^-]}{\text{mol L}^{-1}} = -\log(1.34 \times 10^{-3}) = 2.87$$

From which

$$pH = 14.00 - pOH = 14.00 - 2.87 = 11.13$$

This calculated value checks well with our initial guess.

Occasionally we will find that the approximation

$$c_b - [OH^-] \approx c_b$$

is not valid, in which case we must use a series of successive approximations similar to that outlined above for acids. The appropriate formula can be derived from Equation 5.9.3 and reads

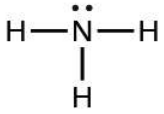
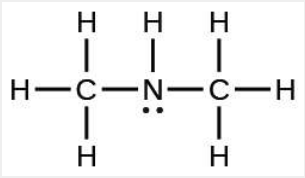
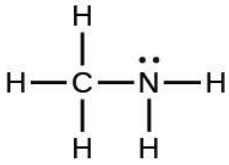
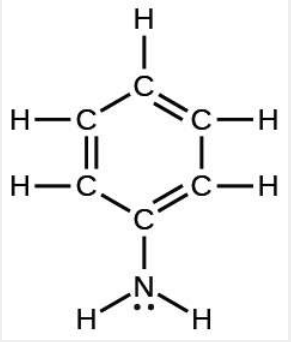
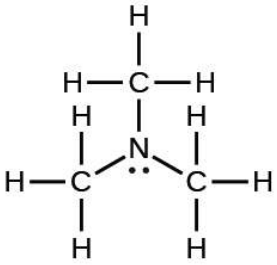
$$[OH^-] \approx \sqrt{K_b(c_b - [OH^-])}$$

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5.10: Ionization Constants of Weak Bases

Ionization Constants of Weak Bases

Ionization Constants of Weak Bases		
Base	Lewis Structure	K_b at 25 °C
ammonia		1.8×10^{-5}
dimethylamine		5.9×10^{-4}
methylamine		4.4×10^{-4}
phenylamine (aniline)		4.3×10^{-10}
trimethylamine		6.3×10^{-5}

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5.11: Relationship Between Ka and Kb

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{5.11.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[HA]} \tag{5.11.2}$$

The equilibrium constant for this reaction is the acid ionization constant K_a, also called the acid dissociation constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{5.11.3}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 5.11.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H^3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them **unitless**. The values of K_a for a number of common acids are given in Table 5.11.1.

Table 5.11.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
*The number in parentheses indicates the ionization step referred to for a polyprotic acid.						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{5.11.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{5.11.5}$$

Once again, the concentration does not appear in the equilibrium constant expression.. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 5.11.2

Table 5.11.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00
*As in Table 5.11.1.						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{5.11.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{5.11.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{5.11.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{5.11.9}$$

If we add Equations 5.11.6 and 5.11.7, we obtain the following (recall that the equilibrium constant for the sum of two reactions is the product of the equilibrium constants for the individual reactions):

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \quad K_a = [H^+]\,[CN^-]/\,[HCN] \tag{5.11.10}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \quad K_b = [OH^-]\,[HCN]/\,[CN^-] \tag{5.11.11}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-] \tag{5.11.12}$$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{5.11.13}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{5.11.14}$$

$$K_a = 10^{-pK_a} \tag{5.11.15}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{5.11.16}$$

$$K_b = 10^{-pK_b} \tag{5.11.17}$$

Similarly, Equation 16.5.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{5.11.18}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{5.11.19}$$

The values of pK_a and pK_b are given for several common acids and bases in Table 16.5.1 and Table 16.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.5. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 16.5.2 are the common strong acids; at the top right are the most common strong bases. **Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.**

> The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base} \tag{5.11.20}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{5.11.21}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO^-_{2\,(aq)}} \tag{5.11.22}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)} \tag{5.11.23}$$

All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

Example 5.11.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.5.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.5.15 and Equation 16.5.16. Use the relationships pK = −log K and K = 10−pK (Equation 16.5.11 and Equation 16.5.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.5.16: pK_a + pK_b = pKw = 14.00. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00 \tag{5.11.24}$$

$$pK_b = 14.00 - 4.83 = 9.17 \tag{5.11.25}$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 16.5.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14} \tag{5.11.26}$$

$$K_a = 1.9 \times 10^{-11} \tag{5.11.27}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27 \tag{5.11.28}$$

$$pKa + pK_b = 14.00 \tag{5.11.29}$$

$$pK_a = 10.73 \tag{5.11.30}$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11} \tag{5.11.31}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 5.11.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

$K_a = 1.4 \times 10^{-4}$ for lactic acid;

pK_b = 10.14 and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

Summary

Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (Ka). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (Kb). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair.

Key Takeaways

- The Ka and Kb values for a conjugated acid–base pairs are related through the K_w value:

$$K_aK_b = K_w \tag{5.11.32}$$

- The conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{5.11.33}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{5.11.34}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w \tag{5.11.35}$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a} \tag{5.11.36}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b} \tag{5.11.37}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w \tag{5.11.38}$$

$$pK_a + pK_b = 14.00 \text{ at } 25^\circ\text{C} \tag{5.11.39}$$

Contributors and Attributions

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5.12: Acid-Base Properties of Salt Solutions

Learning Objectives

- To recognize salts that will produce acidic, basic, or neutral solutions in water
- To understand the Lewis acidity of small, highly-charged metal ions in water

A neutralization reaction can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as Na^+, replaces the proton on the acid. An example is the reaction of CH_3CO_2H, a weak acid, with $NaOH$, a strong base:

$$\underset{\text{acid}}{CH_3CO_2H_{(l)}} + \underset{\text{base}}{NaOH_{(s)}} \xrightarrow{H_2O} \underset{\text{salt}}{H_2OCH_3CO_2Na_{(aq)}} + \underset{\text{water}}{H_2O_{(l)}}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table **5.12.1** and Figure **5.12.1**, we can see that CN^- is a stronger base ($pK_b = 4.79$) than acetate ($pK_b = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Equation 5.12.1). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{5.12.1}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{5.12.2}$$

Equation 5.12.1 indicates that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation and the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Equation 5.12.2, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base (pKa ≈ pKb). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the

cation is a stronger acid than the anion is a base, the final solution has a $pH < 7.00$. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a $pH > 7.00$.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure 5.12.1). A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

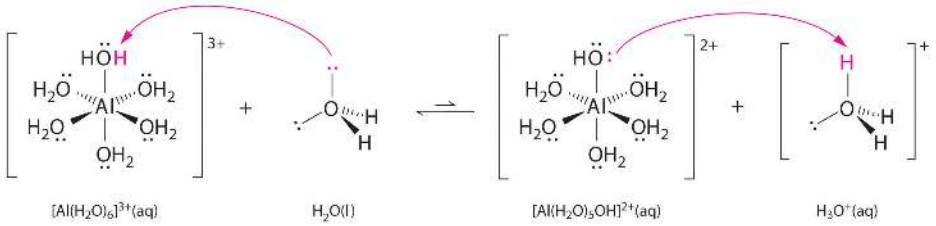


Figure 5.12.1. With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

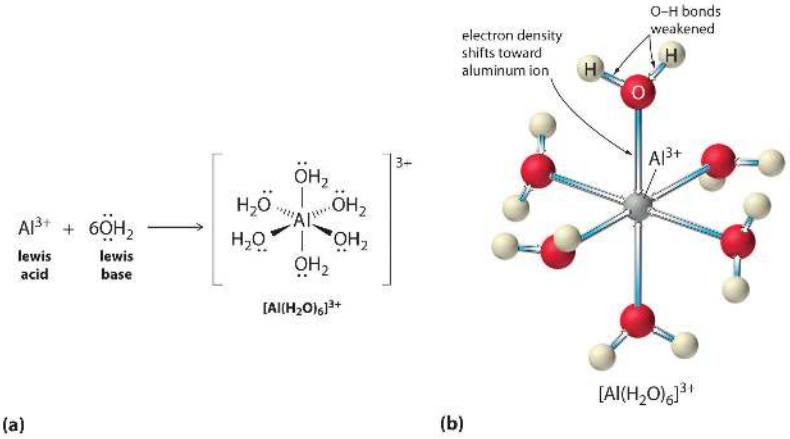


Figure 5.12.1: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

On the left is the reaction of Al three plus with six OH2 which produces [AL(H2O)6] three plus. On the right is the molecular structure of [Al(H2O)6] three plus.

The magnitude of this effect depends on the following two factors (Figure 5.12.2):

1. The charge on the metal ion. A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.
2. The radius of the metal ion. For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

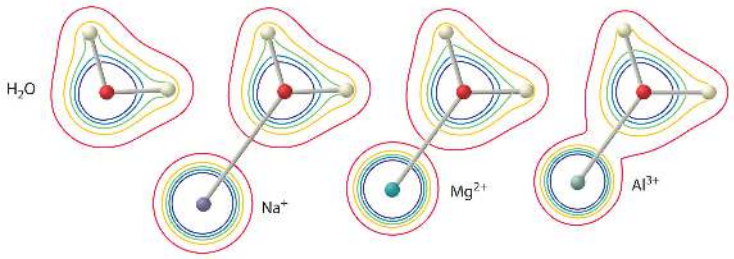


Figure 5.12.2: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{5.12.3}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the charge-to-radius ratio of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+}, have different sizes and charges, but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

> *Solutions of small, highly charged metal ions in water are acidic.*

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

> *A hydrolysis reaction is an acid–base reaction.*

Example 5.12.1

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

a. KNO_3
b. $CrBr_3 cdot H_2O$
c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A. Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.
B. f the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a

A. The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.

B. The NO_3- anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

b.

A. The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[Cr(H2O)_6]^{3+}$ complex, which will behave as a weak acid:

$$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)}$$

B. The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

c.

A. The Na^+ ion, like the K^+, is a very weak acid, so it should not affect the acidity of the solution.
B. In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

Exercise 5.12.1

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

a. KI
b. $Mg(ClO_4)_2$
c. $NaHS$

Answer a

neutral

Answer b

acidic

Answer c

basic (due to the reaction of $\mathbf{HS^-}$ with water to form $\mathbf{H_2S}$ and $\mathbf{OH^-}$)

Summary

A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a hydrolysis reaction.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

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5.13: The Common-Ion Effect

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[Na^+] + [K^+] = [Cl^-] \tag{5.13.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When **NaCl** and **KCl** are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing **NaCl** and **KCl**, the Cl^- ions are common ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$$

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

For example, when **AgCl** is dissolved into a solution already containing **NaCl** (actually Na^+ and Cl^- ions), the Cl^- ions come from the ionization of both **AgCl** and **NaCl**. Thus, $[Cl^-]$ differs from $[Ag^+]$. The following examples show how the concentration of the common ion is calculated.

Example 5.13.1

What are $[Na^+]$, $[Cl^-]$, $[Ca^{2+}]$, and $[H^+]$ in a solution containing 0.10 M each of **NaCl**, $CaCl_2$, and **HCl**?

Solution

Due to the conservation of ions, we have

$$[Na^+] = [Ca^{2+}] = [H^+] = 0.10\ M$$

but

$$\begin{aligned}[Cl^-] = &\ 0.10\ \text{(due to NaCl)} \\ &+ 0.20\ \text{(due to } CaCl_2\text{)} \\ &+ 0.10\ \text{(due to HCl)} \\ = &\ 0.40\ M\end{aligned}$$

Exercise 5.13.1

John poured 10.0 mL of 0.10 M **NaCl**, 10.0 mL of 0.10 M **KOH**, and 5.0 mL of 0.20 M **HCl** solutions together and then he made the total volume to be 100.0 mL. What is $[Cl^-]$ in the final solution?

Solution

$$[Cl^-] = \frac{0.1\ M \times 10\ mL + 0.2\ M \times 5.0\ mL}{100.0\ mL} = 0.020\ M$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 5.13.2: Solubility of Lead Chloride

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \tag{5.13.2}$$

$$= s \times (2s)^2 \tag{5.13.3}$$

$$1.7 \times 10^{-5} = 4s^3 \tag{5.13.4}$$

$$s^3 = \frac{1.7 \times 10^{-5}}{4} \tag{5.13.5}$$

$$= 4.25 \times 10^{-6} \tag{5.13.6}$$

$$s = \sqrt[3]{4.25 \times 10^{-6}} \tag{5.13.7}$$

$$= 1.62 \times 10^{-2}\ mol\ dm^{-3} \tag{5.13.8}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le* Châtelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

Example 5.13.3

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \tag{5.13.9}$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^-] = 0.100\ M \tag{5.13.10}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\,\text{M} \end{aligned} \tag{5.13.11}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{5.13.12}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{5.13.13}$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.



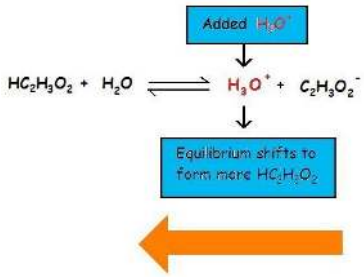
A Video Discussing Finding the Solubility of a Salt: Finding the Solubility of a Salt(opens in new window) [youtu.be]

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

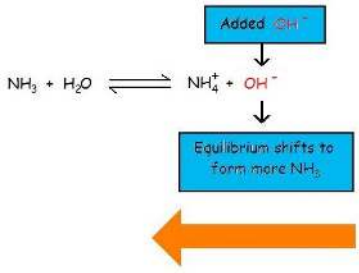
The common ion effect of H_3O^+ on the ionization of acetic acid



HC2H3O2 reactions with H2O to produce H3O plus and C2H3 O2 minus. If more H3O plus is added to the reaction, the equilibrium would shift to form more HC2H3O2.

When a strong acid supplies the common ion $\mathbf{H_3O^+}$ the equilibrium shifts to form more $\mathbf{HC_2H_3O_2}$.

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium. Now consider the common ion effect of $\mathbf{OH^-}$ on the ionization of ammonia



When a strong base supplies the common ion $\mathbf{OH^-}$ the equilibrium shifts to form more $\mathbf{NH_3}$.

NH3 reacts with H2 O to produce NH4 plus and OH minus. If more OH minus is added to the reaction, the equilibrium would shifts to form more NH3.

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq) \tag{5.13.14}$$

As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate. The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[Ca^{2+}]^3[PO_4^{3-}]^2}{[Ca_3(PO_4)_2]} \tag{5.13.15}$$

$$[Ca_3(PO_4)_2]K = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{5.13.16}$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts vary dramatically for different compounds (Table E3). Although K_{sp} is not a function of pH in Equation 5.13.15, changes in pH can affect the solubility of a compound.

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. **Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions.** This dependency is another example of the common ion effect where adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

- $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7} M\ of\ Ca^{2+}$
- $2 \times (1.14 \times 10^{-7} M) = 2.28 \times 10^{-7} M\ of\ PO_4^{3-}$

according to the stoichiometry shown in Equation 5.13.15 (neglecting hydrolysis to form HPO_4^{2-}). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 5.13.15 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

Note

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example 5.13.5

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

What happens to the solubility of $PbCl_2$(s) when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be $(s)(2s)^2 = 1.7\times10^{-5}$. Solving the equation for s gives $s = 1.62\times10^{-2}$ M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$Q_{sp} = [Pb^{2+}][Cl^-]^2 \tag{5.13.17}$$

$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \tag{5.13.18}$$

$$s = [Pb^{2+}] \tag{5.13.19}$$

$$= 1.8 \times 10^{-3} M \tag{5.13.20}$$

$$2s = [Cl^-] \tag{5.13.21}$$

$$\approx 0.1 M \tag{5.13.22}$$

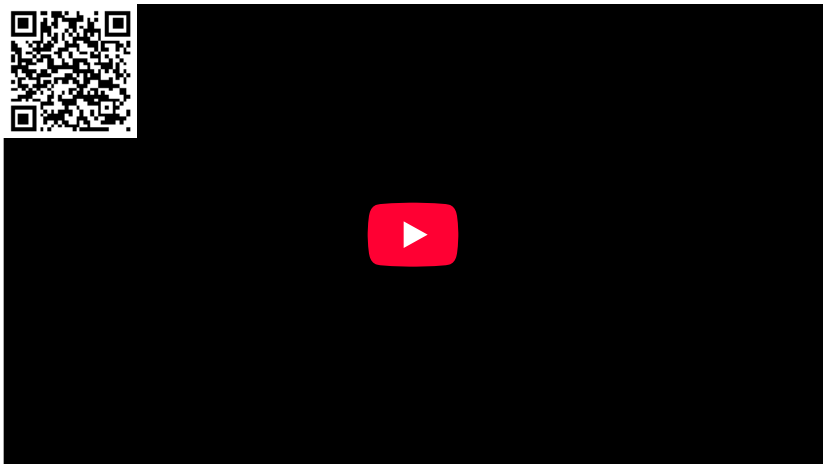
Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

Exercise 5.13.5

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



A Video Discussing the Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products (opens in new window) [youtu.be]

References

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5.14: Buffered 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:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \tag{5.14.1}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \tag{5.14.2}$$

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 5.14.1 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 5.14.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[H^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	−x	+x	+x
Equilibrium	(0.150 − x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_aC_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	−x	+x	+x
final	(0.150 − x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M}$$
$$= 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

? Exercise 5.14.1

A 0.225 M solution of ethylamine ($CH_3CH_2NH_2$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
b. the percentage of ethylamine that is ionized if enough solid $NaOH$ is added to the original solution to give a final concentration of 0.050 M $NaOH$

Answer a

11.16

Answer b

1.3%



A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{5.14.3}$$

If the equilibrium constant for the reaction as written in Equation 5.14.3 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 5.14.3 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:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{5.14.4}$$

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 5.14.4 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 5.14.1, 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.

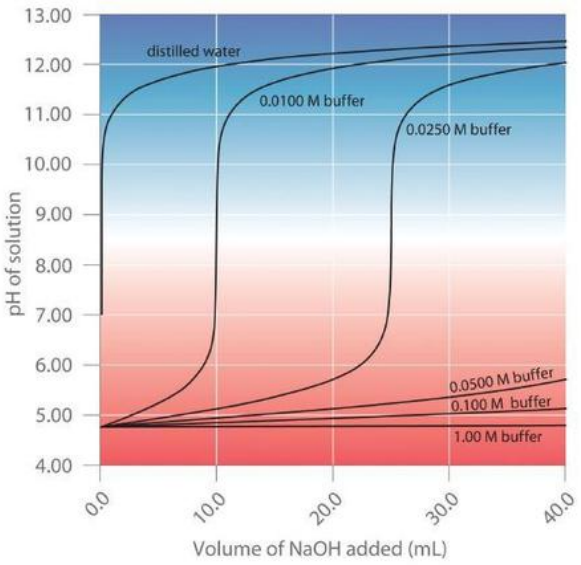


Figure 5.14.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

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 5.14.1 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:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{5.14.5}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{5.14.6}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{5.14.7}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{5.14.8}$$

Replacing the negative logarithms in Equation 5.14.8,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{5.14.9}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{5.14.10}$$

Equation 5.14.9 and Equation 5.14.10 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 5.14.10. 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 5.14.10, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 5.14.10, 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 5.14.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 5.14.9 or 5.14.10) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 5.14.9), 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 5.14.10, 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 5.14.2

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 5.14.9) 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 5.14.3.

Example 5.14.3

The buffer solution in Example 5.14.2 contained 0.135 M $\mathbf{HCO_2H}$ and 0.215 M $\mathbf{HCO_2Na}$ and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M $\mathbf{\mathit{HCl}}$ are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $\mathbf{\mathit{NaOH}}$ 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 5.14.1. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 5.14.10) to obtain the pH.

Solution:

The added $\mathbf{HCl}$ (a strong acid) or $\mathbf{NaOH}$ (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:

$$100\ \cancel{mL}\left(\frac{0.135\ mmol\ \mathbf{HCO_2H}}{\cancel{mL}}\right) = 13.5\ mmol\ \mathbf{HCO_2H}$$

$$100\ \cancel{mL}\left(\frac{0.215\ mmol\ \mathbf{HCO_2^-}}{\cancel{mL}}\right) = 21.5\ mmol\ \mathbf{HCO_2^-}$$

The millimoles of $\mathbf{H^+}$ in 5.00 mL of 1.00 M $\mathbf{HCl}$ is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\ mmol\ \mathbf{H^+}}{\cancel{mL}}\right) = 5\ mmol\ \mathbf{H^+}$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$HCO^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_2H(aq)$$

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 5.14.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 5.14.10):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

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.

$$HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(l)$$

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 5.14.3

The buffer solution from Example 5.14.2 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 **5.14.3** 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 **5.14.2** 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.

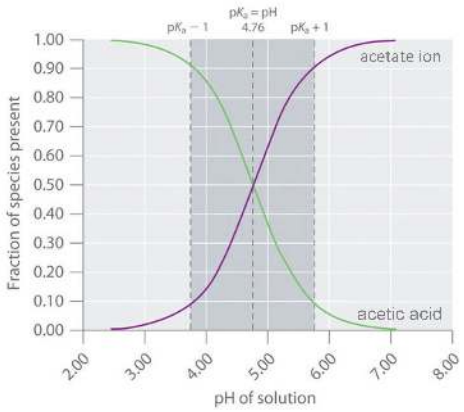


Figure **5.14.2**: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable 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 **5.14.3**. 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.

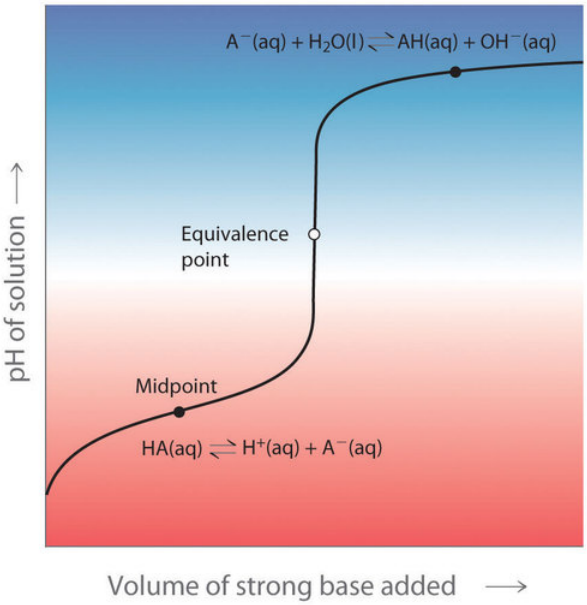


Figure **5.14.3**: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

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:

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{5.14.11}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 5.14.11 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 5.14.11 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 5.14.12, 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:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{5.14.12}$$

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 5.14.11 suggests. Adding Equation 5.14.11 and Equation 5.14.12 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{5.14.13}$$

with $K' = 4.0 \times 10^{-3} (37°C)$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{5.14.14}$$

with $K_a = 2.0 \times 10^{-4} (37°C)$

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{5.14.15}$$

with $K = 8.0 \times 10^{-7} (37°C)$

The K value for the reaction in Equation 5.14.15 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2\,(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{5.14.16}$$

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 5.14.16,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{5.14.17}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 5.14.4 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.

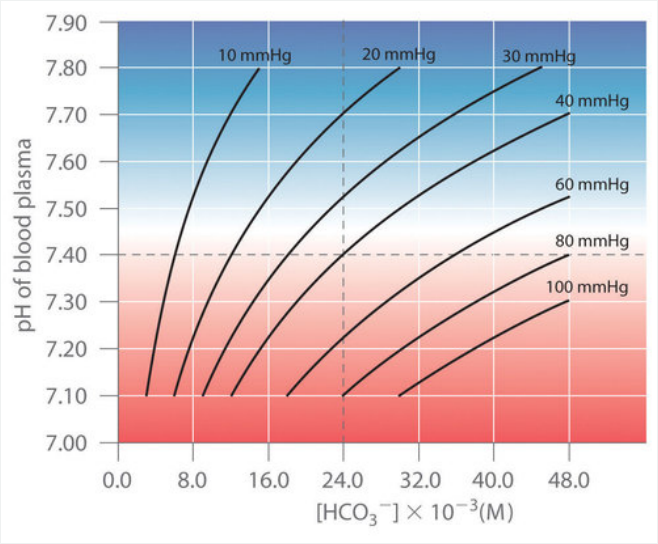


Figure 5.14.4: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 5.14.17, 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 5.14.17 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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5.15: Acid-Base Titrations

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 5.15.1*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 5.15.1*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.

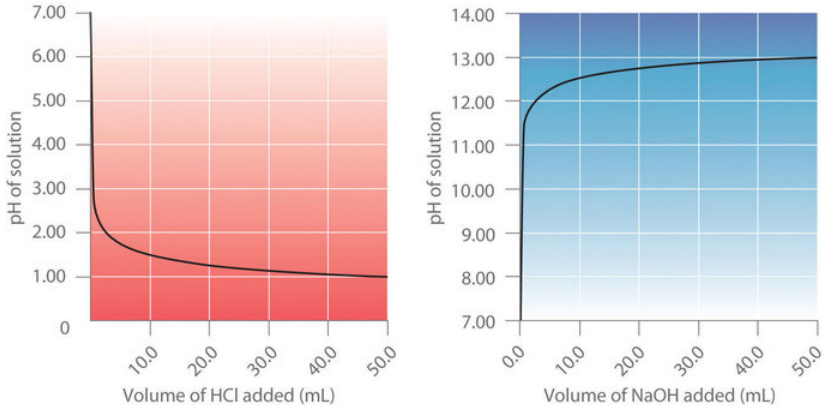


Figure 5.15.1: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 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 5.15.2*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:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \tag{5.15.1}$$

If 0.20 M **NaOH** is added to 50.0 mL of a 0.10 M solution of **HCl**, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

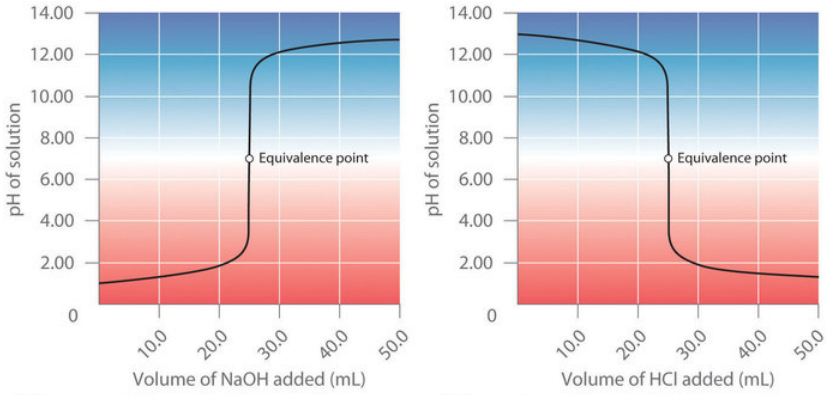


Figure **5.15.2**: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M **NaOH** is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases 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 **5.15.2***b*, 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 **5.15.2***a*. 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 5.15.1: 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 $\mathrm{H^+}$ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00\ \cancel{mL}\left(\frac{0.100\ mmol\ HCl}{\cancel{mL}}\right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90\ \cancel{mL}\left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}}\right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus $\mathrm{H^+}$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $\mathrm{OH^-}$ to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess $\mathrm{H^+}$ is 5.00 mmol − 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $\mathrm{H^+}$ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[\mathrm{H^+}] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Exercise 5.15.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133M$ solution of $NaOH$.

Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, [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, [\(H^+] is less than [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 5.15.3*a* 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 5.15.2. 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.

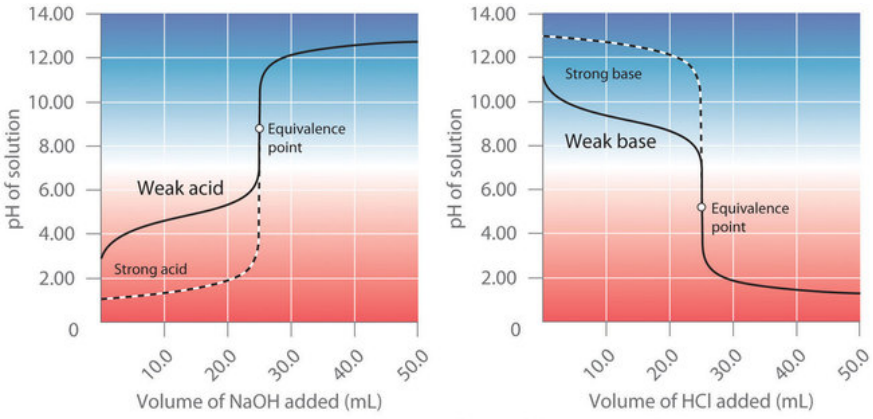


Figure 5.15.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M **NaOH** is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases 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 5.15.3*a* 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 5.15.2 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 $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CO_2{}^-$$

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 $\mathbf{NaOH}$ to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 5.15.3). 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:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{5.15.2}$$

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 $[\mathbf{H^+}]$ 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 $\mathbf{CH_3CO_2H}$ in the original solution and the amount of $\mathbf{OH^-}$ in the $\mathbf{NaOH}$ solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(\mathrm{CH_3CO_2H})/\cancel{mL}) = 5.00\ mmol(\mathrm{CH_3CO_2H})$$

The $\mathbf{NaOH}$ solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H − 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

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

ICE table

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2{}^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[H^+]$ at equilibrium following the addition of $NaOH$, we must first calculate $[CH_3CO_2H]$ and $[CH_3CO_2{}^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

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

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{(1.72 \times 10^{-5})\,(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[H^+]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure 5.15.3*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 5.15.2, 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 5.15.2

What is the pH of the solution after 25.00 mL of 0.200 M **NaOH** is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.

B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.

C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.

D. Calculate K_b using the relationship $K_w = K_aK_b$. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}-\text{mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

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:

$$[CH_3CO_2] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

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

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{5.15.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^-$$

completed table of concentrations

	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 5.15.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} \tag{5.15.4}$$

Substituting the expressions for the final values from the ICE table into Equation 5.15.4 and solving for x:

$$\frac{x^2}{0.0667} = 5.80 \times 10^{-10}$$

$$x = \sqrt{(5.80 \times 10^{-10})(0.0667)}$$

$$= 6.22 \times 10^{-6}$$

Thus $[OH^-] = 6.22 \times 10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure 5.15.3*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 OH^-.

? Exercise 5.15.2

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 **5.15.3**, 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 **5.15.4** 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.

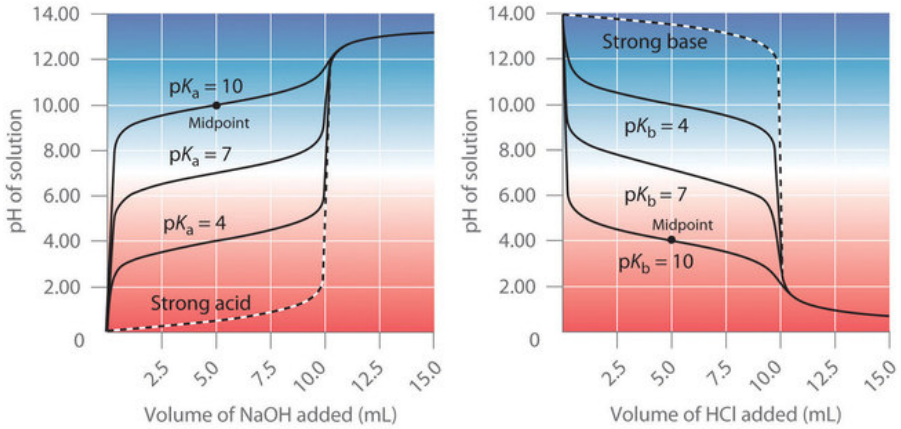


Figure **5.15.4**: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M **NaOH** 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 **5.15.4*a*** and **5.15.4*b*** 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

$$pK_a = pH \tag{5.15.5}$$

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 **5.15.4** 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 5.15.5 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.

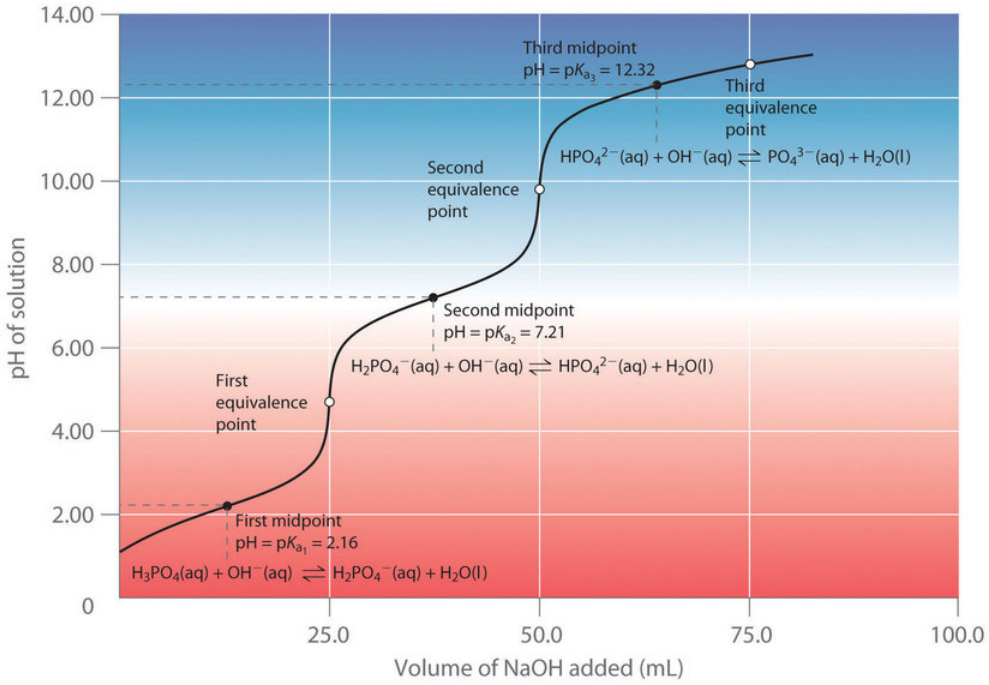
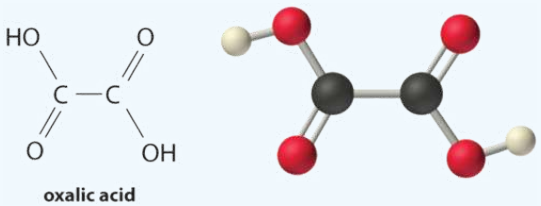


Figure 5.15.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation 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 5.15.5. 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 5.15.3

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 5.15.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}\,[Hox^-]}{[ox^{2-}]} = \frac{(1.6 \times 10^{-4})\,(2.32 \times 10^{-2})}{(9.68 \times 10^{-3})} = 3.7 \times 10^{-4}\ M$$

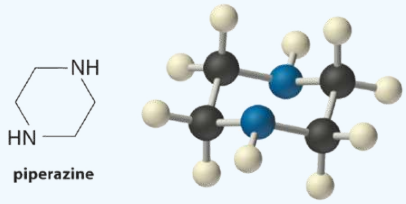
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

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 5.15.3: 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:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{5.15.6}$$

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 5.15.6). 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 5.15.6: 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 5.15.7 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

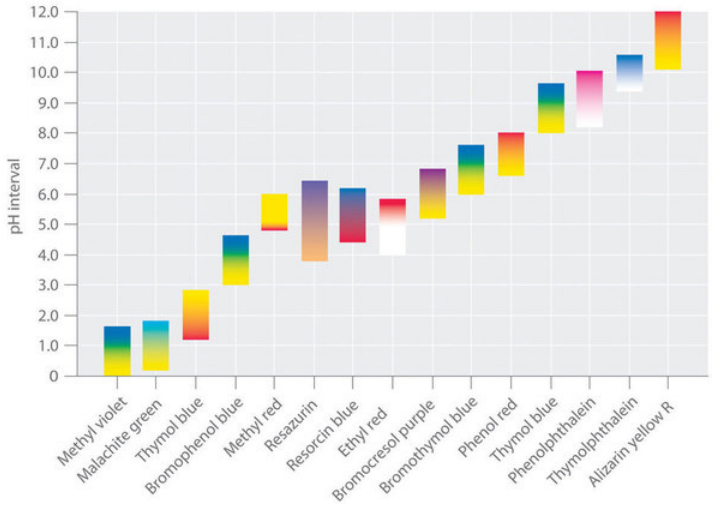


Figure 5.15.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

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 5.15.8. 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.

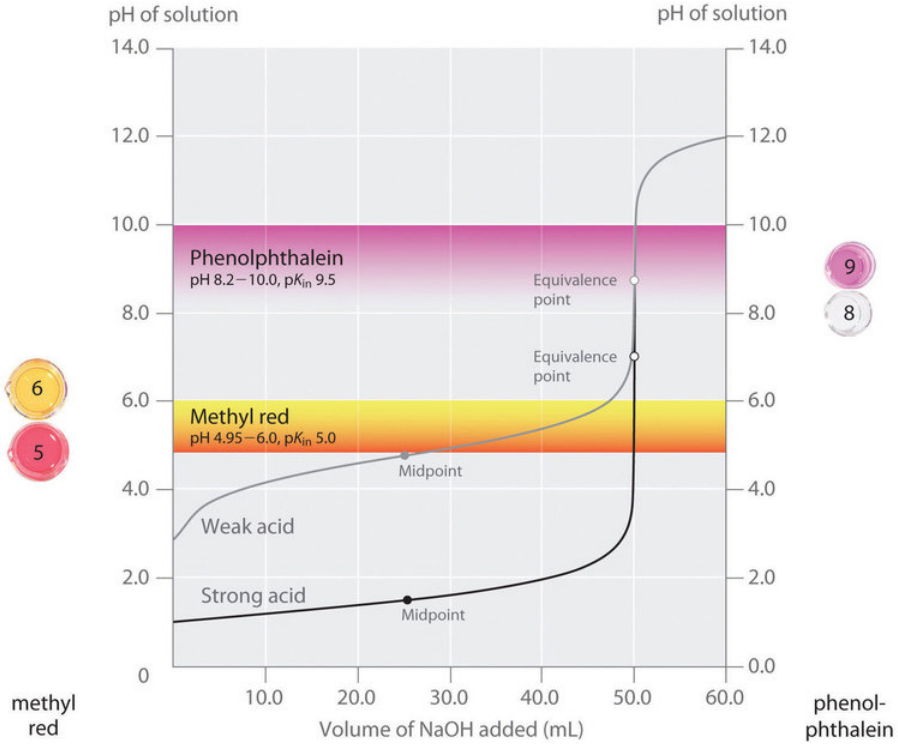


Figure **5.15.8**: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

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 **5.15.9**).

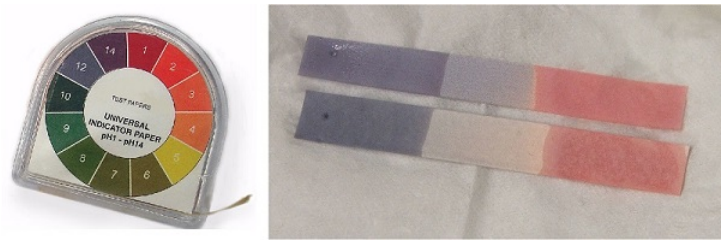


Figure 5.15.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



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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CHAPTER OVERVIEW

6: Electrochemistry

6.1: Oxidation States and Redox Reactions
6.2: Balanced Oxidation-Reduction Equations
6.3: Voltaic Cells
6.4: Cell Potential Under Standard Conditions
6.5: Standard Electrode (Half-Cell) Potentials
6.6: Gibbs Energy and Redox Reactions
6.7: Cell Potential Under Nonstandard Conditions
6.8: Corrosion
6.9: Electrolysis

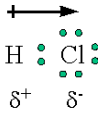
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6.1: Oxidation States and Redox Reactions

Electron transfer is one of the most basic processes that can happen in chemistry. It simply involves the movement of an electron from one atom to another. Many important biological processes rely on electron transfer, as do key industrial transformations used to make valuable products. In biology, for example, electron transfer plays a central role in respiration and the harvesting of energy from glucose, as well as the storage of energy during photosynthesis. In society, electron transfer has been used to obtain metals from ores since the dawn of civilization.

Oxidation States (Numbers)

Oxidation state is a useful tool for keeping track of electron transfers. It is most commonly used in dealing with metals and especially with transition metals. Unlike metals from the first two columns of the periodic table, such as sodium or magnesium, transition metals can often transfer different numbers of electrons, leading to different metal ions (e.g., sodium is generally found as Na^+ and magnesium is almost always Mg^{2+}, but manganese could be Mn^{2+}, Mn^{3+}, and so on, as far as Mn^{7+}). Oxidation state is a number assigned to an element in a compound according to some rules. This number enables us to describe oxidation-reduction reactions, and balancing redox chemical reactions. When a covalent bond forms between two atoms with different electronegativities the shared electrons in the bond lie closer to the more electronegative atom:



For hydrochloric acid, the hydrogen is positive while the chlorine is negative. The dipole starts at the hydrogen and points towards the chlorine.

The **oxidation state** of an atom is the charge that results when the electrons in a covalent bond are assigned to the more electronegative atom and is the charge an atom would possess *if the bonding were ionic*. In HCl (above) the oxidation number for the hydrogen would be +1 and that of the Cl would be -1.

Example 6.1.1

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the Oxidation State of each):

a. $Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$
b. $2\,Al + 3\,Cu^{2+} \rightarrow 2\,Al^{3+} + 3\,Cu$
c. $CO_3^{2-} + 2\,H^+ \rightarrow CO_2 + H_2O$

Solutions

a. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0)
b. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)
c. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

An atom is oxidized if its oxidation number increases, and an atom is reduced if its oxidation number decreases. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation Numbers and Nomenclature

Compounds of the alkali (oxidation number +1) and alkaline earth metals (oxidation number +2) are typically ionic in nature. Compounds of metals with higher oxidation numbers (e.g., tin +4) tend to form molecular compounds

- In ionic and covalent molecular compounds usually the ***less electronegative element is given first***.
- In ionic compounds the names are given which refer to ***the oxidation (ionic) state***
- In molecular compounds the names are given which refer ***to the number of molecules present in the compound***

Figure 6.1.1: Example of nomenclature based on oxidation states.

Ionic		Molecular	
MgH_2	magnesium hydride	H_2S	dihydrogen sulfide
FeF_2	iron(II) fluoride	OF_2	oxygen difluoride
Mn_2O_3	manganese(III) oxide	Cl_2O_3	dichlorine trioxide

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Oxidation-Reduction Reaction Examples

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG,** meaning "*oxidation is loss*" and "*reduction is gain*," and **LEO says GER,** meaning "*loss of* e^- *= oxidation*" and "*gain of* e^- *= reduced*." There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is called the **oxidizing agent**; by accepting electrons it causes the oxidation of another species. Conversely, the species that donates electrons is called the **reducing agent**; when the reaction occurs, it reduces the other species. In other words, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions).



Figure 6.1.1: A thermite reaction taking place on a cast iron skillet. A thermite reaction, using about 110 g of the mixture, taking place. The cast-iron skillet was destroyed in the process. (CC BY-SA 2.5 generic; Schuyler S via Wikipedia).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3 (Figure 6.1.1).

$$Fe_2O_3(s) + 2\,Al(s) \longrightarrow Al_2O_3(s) + 2\,Fe(l)$$

Another example of the redox reaction (although less dangerous) is the reaction between zinc and copper sulfate.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

Example 6.1.2: Identifying Oxidized and Reduced Elements

Determine what is oxidized and what is reduced in the following reaction.

$$Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$$

Solution

The oxidation state of H^+ changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the reducing agent.

The oxidation state of H^+ changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, H^+ ion is reduced and acts as the oxidizing agent.

Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given below:

$$A + B \rightarrow AB$$

Example 6.1.3: Combination Reaction

Equation:

$$H_2 + O_2 \rightarrow H_2O$$

Calculation: 0 + 0 → **(2)(+1) + (-2) = 0**

Explanation:

In this equation both H_2 and O_2 are free elements; following Rule #1, their Oxidation States are 0. The product is H_2O, which has a total Oxidation State of 0. According to Rule #6, the Oxidation State of oxygen is usually -2. Therefore, the Oxidation State of H in H_2O must be +1.

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:

$$AB \rightarrow A + B$$

Example 6.1.4: Decomposition Reaction

Identify the oxidation state of the products and reactant in the decomposition of water:

$$H_2O \rightarrow H_2 + O_2$$

Calculation

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

In this reaction, water is "decomposed" into hydrogen and oxygen. As in the previous example the H_2O has a total Oxidation State of 0; thus, according to Rule #6 the Oxidation State of oxygen is usually -2, so the Oxidation State of hydrogen in H_2O must be +1.

Single Replacement Reactions

A single replacement reaction involves the "replacing" of an element in the reactants with another element in the products:

\[\ce{A + BC \rightarrow AB + C} \nonumber \]

Example 6.1.5: Single Replacement Reaction

Chlorine gas is a great oxidizing agent and will replace bromide ions from sodium bromide salt.

$$Cl_2(g) + NaBr(s) \longrightarrow NaCl(s) + Br_2(l)$$

Explanation

In this equation, Br is replaced with Cl, and the Cl atoms in Cl_2 are reduced, while the Br ion in NaBr is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a single replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

\[\ce{AB + CD \rightarrow AD + CB} \nonumber \]

Example 6.1.6: Double Replacement Reaction

The reaction of gaseous hydrogen chloride and iron oxide is a double replacement reaction. Write the expected reaction for this chemistry equation.

Solution

$$\mathrm{Fe_2O_3 + 6\,HCl \rightarrow 2\,FeCl_3 + 3\,H_2O}$$

In this equation, Fe and H trade places, and oxygen and chlorine trade places.

Combustion Reactions

Combustion reactions almost always involve oxygen in the form of $\mathrm{O_2}$, and are almost always exothermic, meaning they produce heat. Chemical reactions that give off light and heat and light are colloquially referred to as "burning."

$$\mathrm{C_xH_y + O_2 \rightarrow CO_2 + H_2O}$$

Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals "burn" in other environments. For example, both titanium and magnesium burn in nitrogen as well:

$$\mathrm{2\,Ti(s) + N_2(g) \longrightarrow 2\,TiN(s)}$$

$$\mathrm{3\,Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)}$$

Moreover, chemicals can be oxidized by other chemicals than oxygen, such as $\mathrm{Cl_2}$ or $\mathrm{F_2}$; these processes are also considered combustion reactions

Disproportionation Reactions

A single substance can be both oxidized and reduced in some redox reactions. These are known as **disproportionation reactions**, with the following general equation:

$$\mathrm{2\,A \longrightarrow A^{+n} + A^{-n}}$$

where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

Example 6.1.7: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, $\mathrm{H_2O_2}$ poured over a cut. This is a decomposition reaction of hydrogen peroxide (catalyzed by the catalase enzyme) that produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:

$$\mathrm{2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)}$$

Explanation

On the reactant side, H has an Oxidation State of +1 and O has an Oxidation State of -1, which changes to -2 for the product $\mathrm{H_2O}$ (oxygen is reduced), and 0 in the product $\mathrm{O_2}$ (oxygen is oxidized).



Redox Reactions: Redox Reactions(opens in new window) [youtu.be]

Summary

Oxidation signifies a loss of electrons and reduction signifies a gain of electrons. Balancing redox reactions is an important step that changes in neutral, basic, and acidic solutions. The types of redox reactions: Combination and decomposition, Displacement reactions (single and double), Combustion, Disproportionation. The oxidizing agent undergoes reduction and the reducing agent undergoes oxidation.

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6.2: Balanced Oxidation-Reduction Equations

Learning Objectives

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of $Cr^{2+}(aq)$ with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 6.2.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\overset{+2}{\mathrm{Cr}}^{2+}(aq) + \overset{+4}{\mathrm{Mn}}\overset{-2}{\mathrm{O}}_2(aq) + \overset{+1}{\mathrm{H}}^{+}(aq) \rightarrow \overset{+3}{\mathrm{Cr}}^{3+}(aq) + \overset{+2}{\mathrm{Mn}}^{2+}(aq) + \overset{+1}{\mathrm{H}}_2\overset{-2}{\mathrm{O}}(l) \tag{6.2.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$\mathrm{Cr}^{2+} + \mathrm{Mn}^{4+} \longrightarrow \mathrm{Cr}^{3+} + \mathrm{Mn}^{2+} \tag{6.2.2}$$

The oxidation can be written as

$$\underbrace{\mathrm{Cr}^{2+} \longrightarrow \mathrm{Cr}^{3+} + \mathrm{e}^-}_{\text{oxidation with 1 electron lost}} \tag{6.2.3}$$

and the reduction as

$$\underbrace{\mathrm{Mn}^{4+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}}_{\text{reduction with 2 electrons gained}} \tag{6.2.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 6.2.3) by 2 to give

$$2\,\mathrm{Cr}^{2+} \longrightarrow 2\,\mathrm{Cr}^{3+} + 2\,\mathrm{e}^- \tag{6.2.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 6.2.4):

$$2\,\mathrm{Cr}^{2+} \rightarrow 2\,\mathrm{Cr}^{3+} + 2\,\mathrm{e}^-$$

$$\mathrm{Mn}^{4+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Mn}^{2+}$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2\,\mathrm{Cr}^{2+} \rightarrow 2\,\mathrm{Cr}^{3+} + \cancel{2\,\mathrm{e}^-}$$

$$\mathrm{Mn}^{4+} + \cancel{2\,\mathrm{e}^-} \rightarrow \mathrm{Mn}^{2+}$$

to result in the balanced redox reaction (metals only)

$$\mathrm{Mn^{4+} + 2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + Mn^{2+}} \tag{6.2.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$\mathrm{MnO_2(aq) + 2\,Cr^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + Mn^{2+}(aq)} \tag{6.2.7}$$

> *In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 6.2.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add $\mathrm{H^+}$ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding $\mathrm{OH^-}$ as necessary to either side of the equation to balance the charges.

In this case, adding four $\mathrm{H^+}$ ions to the left side of Equation 6.2.7 to give

$$\mathrm{MnO_2(s) + 2\,Cr^{2+}(aq) + 4\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + Mn^{2+}(aq)} \tag{6.2.8}$$

Although the charges are now balanced in Equation 6.2.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding $\mathrm{H_2O}$ as necessary to either side of the equation. Here, we need to add two $\mathrm{H_2O}$ molecules to the right side of Equation 6.2.8:

$$\mathrm{MnO_2(s) + 2\,Cr^{2+}(aq) + 4\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + Mn^{2+}(aq) + 2\,H_2O(l)} \tag{6.2.9}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example 6.2.1 below.

Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding $\mathrm{H_2O}$ molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

Example 6.2.1: Balancing in Acid Solutions

Arsenic acid ($\mathrm{H_3AsO_4}$) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine ($\mathrm{AsH_3}$, a highly toxic and unstable gas) and $\mathrm{Zn^{2+}(aq)}$. Balance the equation for this reaction using oxidation states:

$$\mathrm{H_3AsO_4(aq) + Zn(s) \longrightarrow AsH_3(g) + Zn^{2+}(aq)}$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. *Write a chemical equation showing the reactants and the products.* Because we are given this information, we can skip this step.
2. *Assign oxidation states and determine which atoms change oxidation state.* The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$\overset{+5}{H_3As}O_4(aq) + \overset{0}{Zn}(s) \rightarrow \overset{-3}{As}H_3(g) + \overset{+2}{Zn^{2+}}(aq)$$

3. *Write separate equations for oxidation and reduction.* The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\underbrace{\overset{+5}{As} + 8e^- \rightarrow \overset{-3}{As}}_{\text{Reduction with gain of 8 electrons}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\underbrace{\overset{0}{Zn} \rightarrow \overset{+2}{Zn^{2+}} + 2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. *Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.* The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\begin{aligned} \overset{+5}{\text{As}} + 8\,\text{e}^- &\rightarrow \overset{-3}{\text{As}} \\ 4\,\overset{0}{\text{Zn}} &\rightarrow 4\,\overset{+2}{\text{Zn}^{2+}} + 8\,\text{e}^- \end{aligned}$$

5. *Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.* Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives
   - Reduction:

$$\text{H}_3\text{AsO}_4(\text{aq}) + 8\,\text{e}^- \rightarrow \text{AsH}_3(\text{g})$$

   - Oxidation:

$$4\,\text{Zn(s)} \longrightarrow 4\,\text{Zn}^{2+}(\text{aq}) + 8\,\text{e}^-$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$\text{H}_3\text{AsO}_4(\text{aq}) + 4\,\text{Zn(s)} + \cancel{8\,\text{e}^-} \rightarrow \text{AsH}_3(\text{g}) + 4\,\text{Zn}^{2+}(\text{aq}) + \cancel{8\,\text{e}^-}$$

which then yields after canceling electrons

$$\text{H}_3\text{AsO}_4(\text{aq}) + 4\,\text{Zn(s)} \rightarrow \text{AsH}_3(\text{g}) + 4\,\text{Zn}^{2+}(\text{aq})$$

7. *Balance the charge by adding* H^+ *or* OH^- *ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$\text{H}_3\text{AsO}_4(\text{aq}) + 4\,\text{Zn(s)} + 8\,\text{H}^+(\text{aq}) \rightarrow \text{AsH}_3(\text{g}) + 4\,\text{Zn}^{2+}(\text{aq})$$

8. *Balance the oxygen atoms by adding* H_2O *molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 H_2O molecules to the right side balances the O atoms:

$$\text{H}_3\text{AsO}_4(\text{aq}) + 4\,\text{Zn(s)} + 8\,\text{H}^+(\text{aq}) \rightarrow \text{AsH}_3(\text{g}) + 4\,\text{Zn}^{2+}(\text{aq}) + 4\,\text{H}_2\text{O(l)}$$

Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
   - Atoms:

$$1\,\text{As} + 4\,\text{Zn} + 4\,\text{O} + 11\,\text{H} \overset{\checkmark}{=} 1\,\text{As} + 4\,\text{Zn} + 4\,\text{O} + 11\,\text{H}$$

   - Charge:

$$8(+1) \overset{\checkmark}{=} 4(+2)$$

The balanced chemical equation (both for charge and for atoms) for this reaction is therefore:

$$\text{H}_3\text{AsO}_4(\text{aq}) + 4\,\text{Zn}(\text{s}) + 8\,\text{H}^+(\text{aq}) \longrightarrow \text{AsH}_3(\text{g}) + 4\,\text{Zn}^{2+}(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l})$$

? Exercise 6.2.1: Oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$\text{CuS}(\text{s}) + \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{NO}(\text{g}) + \text{SO}_4^{2-}(\text{aq})$$

Answer

$$3\,\text{CuS}(\text{s}) + 8\,\text{H}^+(\text{aq}) + 8\,\text{NO}_3^-(\text{aq}) \rightarrow 3\,\text{Cu}^{2+}(\text{aq}) + 8\,\text{NO}(\text{g}) + 3\,\text{SO}_4^{2-}(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l})$$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 6.2.2.

✔ Example 6.2.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$\text{Al}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow [\text{Al}(\text{OH})_4]^-(\text{aq}) + \text{H}_2(\text{g})$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example 6.2.1, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic *Al* to +3 in $[\text{Al}(\text{OH})_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in H_2. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}_{(s)} + \overset{+1}{H}_2O_{(aq)} \rightarrow [\overset{+3}{Al}(OH)_4]^-_{(aq)} + \overset{0}{H}_{2(g)}$$

3. Write separate equations for oxidation and reduction.
   - Reduction:

$$\overset{+1}{H} + e^- \rightarrow \overset{0}{H}\ (in\ H_2)$$

   - Oxidation:

$$\overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
   - Reduction:

$$3\,\mathrm{H^+} + 3\,\mathrm{e^-} \longrightarrow 3\,\mathrm{H^0}\ (in\ \mathrm{H_2})$$

   - Oxidation:

$$\mathrm{Al^0} \longrightarrow \mathrm{Al^{3+}} + 3\,\mathrm{e^-}$$

5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of $\mathrm{H_2O}$ contains two protons, in this case, $3\,\mathrm{H^+}$ corresponds to $\frac{3}{2}\mathrm{H_2O}$. Similarly, each molecule of hydrogen gas contains two H atoms, so 3 H corresponds to $\frac{3}{2}\mathrm{H_2}$.
   - Reduction:

$$\tfrac{3}{2}\mathrm{H_2O} + 3\,\mathrm{e^-} \longrightarrow \tfrac{3}{2}\mathrm{H_2}$$

   - Oxidation:

$$\mathrm{Al} \longrightarrow [\mathrm{Al(OH)_4}]^- + 3\,\mathrm{e^-}$$

6. Adding the equations and canceling the electrons gives

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2O} + \cancel{3\,\mathrm{e^-}} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\mathrm{H_2} + \cancel{3\,\mathrm{e^-}}$$

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2O} \longrightarrow [\mathrm{Al(OH)_4}]^- + \tfrac{3}{2}\mathrm{H_2}$$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2\,\mathrm{Al} + 3\,\mathrm{H_2O} \rightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two $\mathrm{OH^-}$ ions to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 3\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three $\mathrm{H_2O}$ molecules to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH^-} + 6\,\mathrm{H_2O} \longrightarrow 2\,[\mathrm{Al(OH)_4}]^- + 3\,\mathrm{H_2}$$

9. Be sure the equation is balanced:
   1. Atoms:

$$2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H} \overset{\checkmark}{=} 2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H}$$

   2. Charge:

$$(2)(0) + (2)(-1) + (6)(0) \overset{\checkmark}{=} (2)(-1) + (3)(0)$$

The balanced chemical equation is therefore

$$2\,\mathrm{Al(s)} + 2\,\mathrm{OH^-(aq)} + 6\,\mathrm{H_2O(l)} \rightarrow 2\,[\mathrm{Al(OH)_4}]^-\mathrm{(aq)} + 3\,\mathrm{H_2(g)}$$

Thus 3 mol of H_2 gas are produced for every 2 mol of Al consumed.

? Exercise 6.2.2: Reducing Manganese in permanganate

The permanganate ion reacts with nitrite ion in basic solution to produce manganese (IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer

$$2\,MnO_4^-(aq) + 3\,NO_2^-(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + 3\,NO_3^-(aq) + 2\,OH^-(aq)$$

As suggested in Examples 6.2.1 and 6.2.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^-, NO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4, NH_3, H_2S, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> *Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.*



Balancing a Redox Reaction in Acidic Conditions: Balancing a Redox Reaction in Acidic Conditions (opens in new window) [youtu.be]

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

Contributors and Attributions

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6.3: Voltaic Cells

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 6.3.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 6.3.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

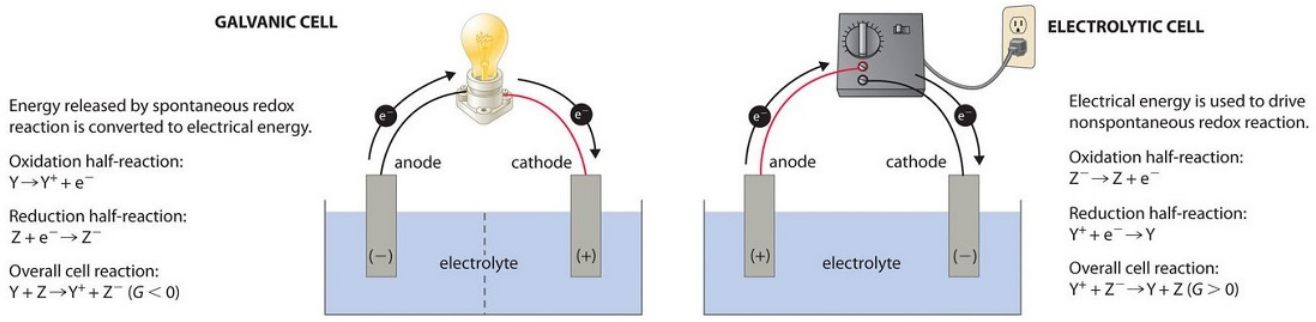


Figure 6.3.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$\mathrm{Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)} \tag{6.3.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure 6.3.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $Zn^{2+}(aq)$ ions, while $Cu^{2+}(aq)$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure $6.3.3a$. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the

circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 6.3.3*b*). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

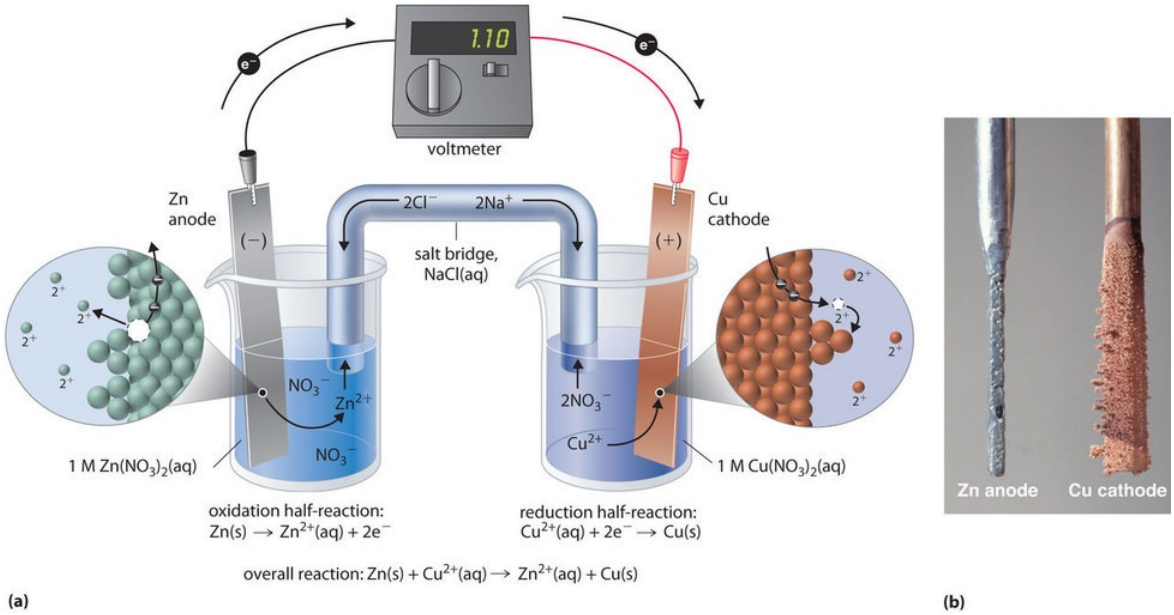


Figure 6.3.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 6.3.3*a*). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 6.3.1.

> *A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

Example 6.3.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,\mathrm{Sn(s)} + 2\,\mathrm{NO_3^-(aq)} + 8\,\mathrm{H^+(aq)} \rightarrow 3\,\mathrm{Sn^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form $\mathrm{NO_2}$, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$\mathrm{NO_3^-(aq)} + 4\,\mathrm{H^+(aq)} + 3\,\mathrm{e^-} \rightarrow \mathrm{NO(g)} + 2\,\mathrm{H_2O(l)}$$

oxidation:

$$\mathrm{Sn(s)} \rightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-}$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to $\mathrm{Sn^{2+}}$.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

Exercise 6.3.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of $\mathrm{MnO_4^-}$ in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of $\mathrm{Sn^{2+}}$ in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,\mathrm{MnO_4^-(aq)} + 5\,\mathrm{Sn^{2+}(aq)} + 16\,\mathrm{H^+(aq)} \rightarrow 2\,\mathrm{Mn^{2+}(aq)} + 5\,\mathrm{Sn^{4+}(aq)} + 8\,\mathrm{H_2O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

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

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.



Electrochemical Cells: Electrochemical Cells(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the $\mathrm{Zn/Cu}$ cell shown in Figure $6.3.3a$ is written as follows:

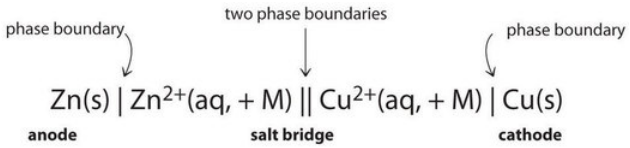


Figure 6.3.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\mathrm{Pt(s)\,|\,H_2(g)|HCl(aq,\ 1\ M)\,|\,AgCl(s)\,Ag(s)}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

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

anode reaction:

$$\mathrm{\tfrac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 6.3.2

Draw a cell diagram for the galvanic cell described in Example 6.3.1. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\,|\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise 6.3.2

Draw the cell diagram for the following reaction, assuming the concentration of $\mathrm{Ag^+}$ and $\mathrm{Mg^{2+}}$ are each 1 M:

$$\mathrm{Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)}$$

Answer

$$\mathrm{Mg(s)\,|\,Mg^{2+}(aq,\ 1\ M)\,||\,Ag^+(aq,\ 1\ M)\,|\,Ag(s)}$$



Cell Diagrams: Cell Diagrams(opens in new window) [youtu.be]

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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6.4: Cell Potential Under Standard Conditions

Learning Objectives

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

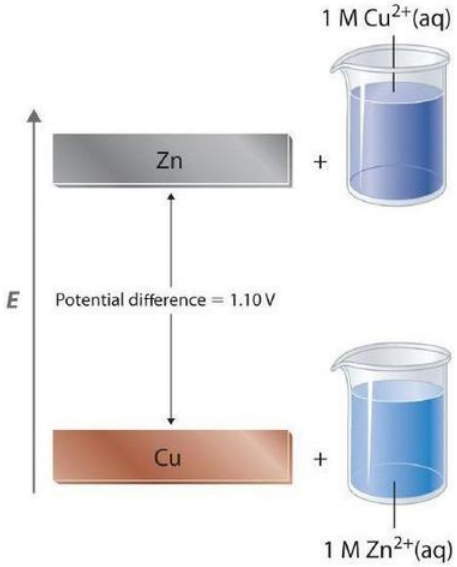


Figure **6.4.1**: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic ***Zn*** and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous ***Zn^{2+}*** ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure **6.4.1** but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E° = 0.59\ V \tag{6.4.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{6.4.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 6.4.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

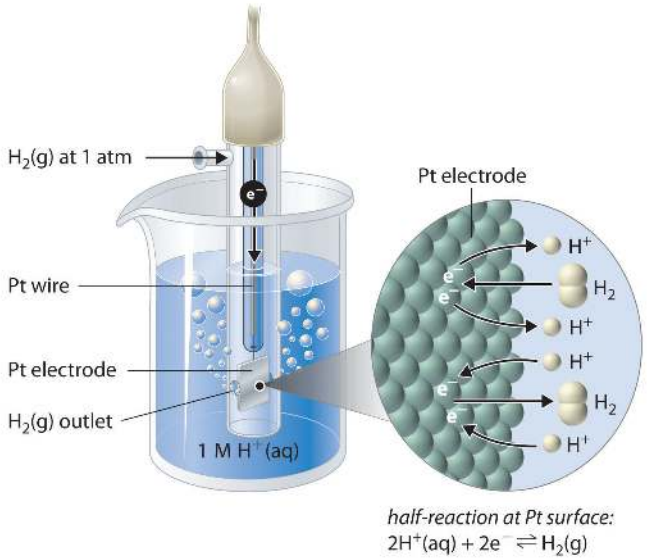


Figure 6.4.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 6.4.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{6.4.3}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

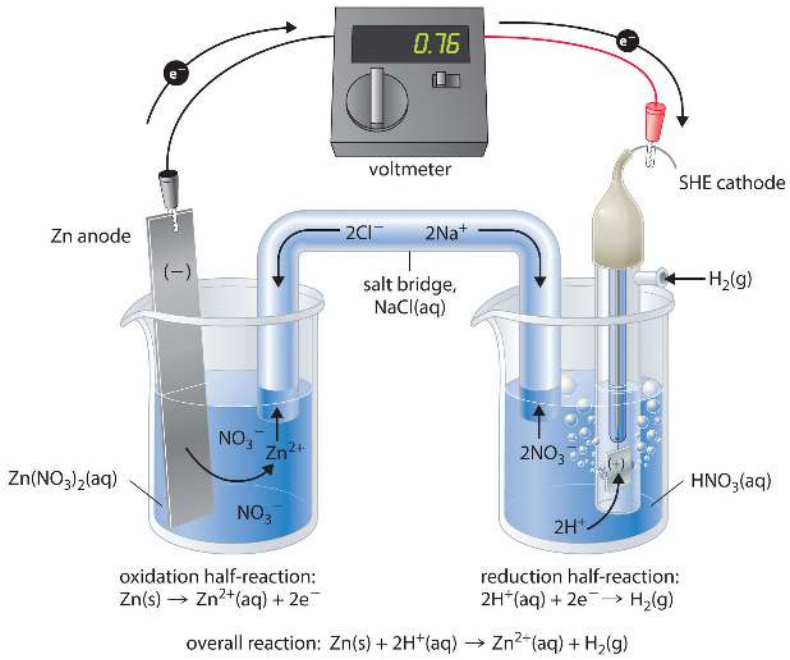


Figure **6.4.3**: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure **6.4.3** shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{6.4.4}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{6.4.5}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{6.4.6}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{6.4.7}$$

We then use Equation 6.4.2 to calculate the cell potential

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= 0.76\ V \end{aligned}$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E°_{cell} : 0\,V - (-0.76\,V) = 0.76\,V$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*



The Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE)(opens in new window) [youtu.be]

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure **6.4.3** but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\,M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{6.4.8}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\,V \tag{6.4.9}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\,V \tag{6.4.10}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{6.4.11}$$

We then use Equation 6.4.2 to calculate the cell potential

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$= 0.34\,V$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.



Electrode Potentials and ECell: Electrode and Potentials and Ecell(opens in new window) [youtu.be]

Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{6.4.12}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to $H_2$and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{6.4.13}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{6.4.14}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 6.4.13, two H^+ ions gain one electron each in the reduction; in Equation 6.4.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 6.4.13) by 3 and the oxidation half-reaction (Equation 6.4.14) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{6.4.15}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{6.4.16}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{6.4.17}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{6.4.18}$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{6.4.19}$$

The atoms also balance, so Equation 6.4.18 is a balanced chemical equation for the redox reaction depicted in Equation 6.4.12.

> *The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 6.4.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{6.4.20}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{6.4.21}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{6.4.22}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{6.4.23}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{6.4.24}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{6.4.25}$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{6.4.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{6.4.27}$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 6.4.26 (the reductive half-reaction) by 3 and Equation 6.4.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{6.4.28}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{6.4.29}$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{6.4.30}$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{6.4.31}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 6.4.31 is identical to Equation 6.4.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 6.4.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}(aq)$ complex and brown $I_2(aq)$ ions (Figure 6.4.4):

$$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Table P1

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:

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

- oxidation:

$$2\,I^-\,(aq) \longrightarrow I_2\,(aq) + 2\,e^-$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$6\,I^-\,(aq) \longrightarrow 3\,I_2\,(aq) + 6\,e^-$$

Adding the two half-reactions and canceling electrons,

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,I^-\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l) + 3\,I_2\,(aq)$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$
$$+6 \overset{\checkmark}{=} +6$$

and atoms

$$2\,Cr + 7\,O + 14\,H + 6\,I \overset{\checkmark}{=} 2\,Cr + 7\,O + 14\,H + 6\,I$$

Both the charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from Cr^{6+} in $Cr_2O_7^{2-}$ to Cr^{3+}, and I^- ions are oxidized to I_2. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O_{7(aq)}^{2-} \rightarrow Cr_{(aq)}^{3+}$$

- oxidation:

$$I_{(aq)}^- \rightarrow I_{2(aq)}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O_{7(aq)}^{2-} \rightarrow 2Cr_{(aq)}^{3+}$$

- oxidation:

$$2I_{(aq)}^- \rightarrow I_{2(aq)}$$

We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$Cr_2O_{7(aq)}^{2-} \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}$$

Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O_{7(aq)}^{2-} + 14H_{(aq)}^+ \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$\mathrm{Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,I^-\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l) + 3\,I_2\,(aq)}$$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

? Exercise 6.4.1

Copper is found as the mineral covellite (**CuS**). The first step in extracting the copper is to dissolve the mineral in nitric acid ($\mathbf{HNO_3}$), which oxidizes sulfide to sulfate and reduces nitric acid to **NO**:

$$\mathrm{CuS\,(s) + HNO_3\,(aq) \rightarrow NO\,(g) + CuSO_4\,(aq)}$$

Balance this equation using the half-reaction method.



Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer

$$\mathrm{3\,CuS\,(s) + 8\,HNO_3\,(aq) \longrightarrow 8\,NO\,(g) + 3\,CuSO_4\,(aq) + 4\,H_2O\,(l)}$$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{6.4.32}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{6.4.33}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{6.4.34}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{6.4.35}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example **6.4.2** and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

Example 6.4.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$\text{cathode: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B. Use Equation 6.4.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 6.4.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$0.27\,V = E°°_{cathhode} - (-0.55\,V)$$

$$E°_{cathode} = -0.28\,V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\text{ V}) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

Exercise 6.4.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$

- anode: $\mathrm{Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-}$

If the potential for the oxidation of Mg to $\mathrm{Mg^{2+}}$ is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

Answer

0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{6.4.36}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure **6.4.5**. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{6.4.37}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{6.4.38}$$

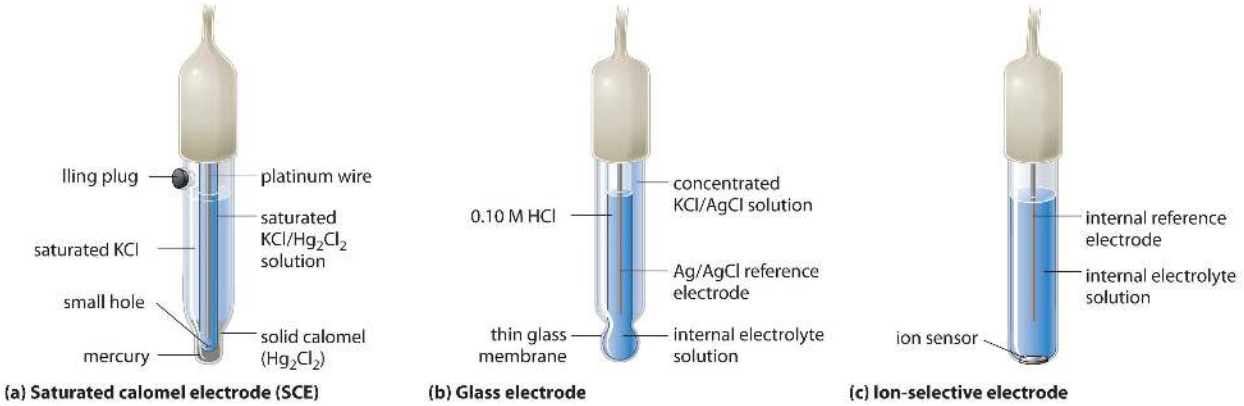


Figure **6.4.5**: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure **6.4.5**. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that $pH = -\log[H^+]$):

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{6.4.39}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure **6.4.5**). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table **6.4.1**.

Table **6.4.1**: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} − E°_{anode} \nonumber \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

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6.5: Standard Electrode (Half-Cell) Potentials

Standard Electrode (Half-Cell) Potentials

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Half-Reaction	$E°$ (V)
$Ag^+ + e^- \longrightarrow Ag$	+0.7996
$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.22233
$[Ag(CN)_2]^- + e^- \longrightarrow Ag + 2\,CN^-$	−0.31
$Ag_2CrO_4 + 2\,e^- \longrightarrow 2\,Ag + CrO_4^{2-}$	+0.45
$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2\,NH_3$	+0.373
$[Ag(S_2O_3)_2]^{3+} + e^- \longrightarrow Ag + 2\,S_2O_3^{2-}$	+0.017
$[AlF_6]^{3-} + 3\,e^- \longrightarrow Al + 6\,F^-$	−2.07
$Al^{3+} + 3\,e^- \longrightarrow Al$	−1.662
$Am^{3+} + 3\,e^- \longrightarrow Am$	−2.048
$Au^{3+} + 3\,e^- \longrightarrow Au$	+1.498
$Au^+ + e^- \longrightarrow Au$	+1.692
$Ba^{2+} + 2\,e^- \longrightarrow Ba$	−2.912
$Be^{2+} + 2\,e^- \longrightarrow Be$	−1.847
$Br_2(aq) + 2\,e^- \longrightarrow 2\,Br^-$	+1.0873
$Ca^{2+} + 2\,e^- \longrightarrow Ca$	−2.868
$Ce^3 + 3\,e^- \longrightarrow Ce$	−2.483
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61
$Cd^{2+} + 2\,e^- \longrightarrow Cd$	−0.4030
$[Cd(CN)_4]^{2-} + 2\,e^- \longrightarrow Cd + 4\,CN^-$	−1.09
$[Cd(NH_3)_4]^{2+} + 2\,e^- \longrightarrow Cd + 4\,NH_3$	−0.61
$CdS + 2\,e^- \longrightarrow Cd + S^{2-}$	−1.17
$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$	+1.35827
$ClO_4^- + H_2O + 2\,e^- \longrightarrow ClO_3^- + 2\,OH^-$	+0.36
$ClO_3^- + H_2O + 2\,e^- \longrightarrow ClO_2^- + 2\,OH^-$	+0.33
$ClO_2^- + H_2O + 2\,e^- \longrightarrow ClO^- + 2\,OH^-$	+0.66
$ClO^- + H_2O + 2\,e^- \longrightarrow Cl^- + 2\,OH^-$	+0.89
$ClO_4^- + 2\,H_3O^+ + 2\,e^- \longrightarrow ClO_3^- + 3\,H_2O$	+1.189
$ClO_3^- + 3\,H_3O^+ + 2\,e^- \longrightarrow HClO_2 + 4\,H_2O$	+1.21
$HClO + H_3O^+ + 2\,e^- \longrightarrow Cl^- + 2\,H_2O$	+1.482
$HClO + H_3O^+ + e^- \longrightarrow \frac{1}{2}Cl_2 + 2\,H_2O$	+1.611
$HClO_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow HClO + 3\,H_2O$	+1.628
$Co^{3+} + e^- \longrightarrow Co^{2+}\ \ (2\,mol\,//\,H_2SO_4)$	+1.83

Half-Reaction	$E°$ (V)
$\mathrm{Co^{2+} + 2\,e^- \longrightarrow Co}$	−0.28
$\mathrm{[Co(NH_3)_6]^{3+} + e^- \xrightarrow{Co(NH_3)_6} {}^{2}+}$	+0.1
$\mathrm{Co(OH)_3 + e^- \longrightarrow Co(OH)_2 + OH^-}$	+0.17
$\mathrm{Cr^3 + 3\,e^- \longrightarrow Cr}$	−0.744
$\mathrm{Cr^{3+} + e^- \longrightarrow Cr^{2+}}$	−0.407
$\mathrm{Cr^{2+} + 2\,e^- \longrightarrow Cr}$	−0.913
$\mathrm{[Cu(CN)_2]^- + e^- \longrightarrow Cu + 2\,CN^-}$	−0.43
$\mathrm{CrO_4^{2-} + 4\,H_2O + 3\,e^- \longrightarrow Cr(OH)_3 + 5\,OH^-}$	−0.13
$\mathrm{Cr_2O_7^{2-} + 14\,H_3O^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 21\,H_2O}$	+1.232
$\mathrm{[Cr(OH)_4]^- + 3\,e^- \longrightarrow Cr + 4\,OH^-}$	−1.2
$\mathrm{Cr(OH)_3 + 3\,e^- \longrightarrow Cr + 3\,OH^-}$	−1.48
$\mathrm{Cu^{2+} + e^- \longrightarrow Cu^+}$	+0.153
$\mathrm{Cu^{2+} + 2\,e^- \longrightarrow Cu}$	+0.34
$\mathrm{Cu^+ + e^- \longrightarrow Cu}$	+0.521
$\mathrm{F_2 + 2\,e^- \longrightarrow 2\,F^-}$	+2.866
$\mathrm{Fe^{2+} + 2\,e^- \longrightarrow Fe}$	−0.447
$\mathrm{Fe^{3+} + e^- \longrightarrow Fe^{2+}}$	+0.771
$\mathrm{[Fe(CN)_6]^{3-} + e^- \xrightarrow{Fe(CN)_6} {}^{4-}}$	+0.36
$\mathrm{Fe(OH)_2 + 2\,e^- \longrightarrow Fe + 2\,OH^-}$	−0.88
$\mathrm{FeS + 2\,e^- \longrightarrow Fe + S^{2-}}$	−1.01
$\mathrm{Ga^{3+} + 3\,e^- \longrightarrow Ga}$	−0.549
$\mathrm{Gd^{3+} + 3\,e^- \longrightarrow Gd}$	−2.279
$\mathrm{\frac{1}{2}H_2 + e^- \longrightarrow H^-}$	−2.23
$\mathrm{2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-}$	−0.8277
$\mathrm{H_2O_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow 4\,H_2O}$	+1.776
$\mathrm{2\,H_3O^+ + 2\,e^- \longrightarrow H_2 + 2\,H_2O}$	0.00
$\mathrm{HO_2^- + H_2O + 2\,e^- \longrightarrow 3\,OH^-}$	+0.878
$\mathrm{Hf^{4+} + 4\,e^- \longrightarrow Hf}$	−1.55
$\mathrm{Hg^{2+} + 2\,e^- \longrightarrow Hg}$	+0.851
$\mathrm{2\,Hg^{2+} + 2\,e^- \longrightarrow Hg_2^{2+}}$	+0.92
$\mathrm{Hg_2^{2+} + 2\,e^- \longrightarrow 2\,Hg}$	+0.7973
$\mathrm{[HgBr_4]^{2-} + 2\,e^- \longrightarrow Hg + 4\,Br^-}$	+0.21

Half-Reaction	$E°$ (V)
$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.26808
$[Hg(CN)_4]^{2-} + 2e^- \longrightarrow Hg + 4CN^-$	−0.37
$[HgI_4]^{2-} + 2e^- \longrightarrow Hg + 4I^-$	−0.04
$HgS + 2e^- \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2e^- \longrightarrow 2I^-$	+0.5355
$In^{3+} + 3e^- \longrightarrow In$	−0.3382
$K^+ + e^- \longrightarrow K$	−2.931
$La^{3+} + 3e^- \longrightarrow La$	−2.52
$Li^+ + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3e^- \longrightarrow Lu$	−2.28
$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.185
$MnO_2 + 2H_2O + 2e^- \longrightarrow Mn(OH)_2 + 2OH^-$	−0.05
$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$	+0.558
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.507
$Na^+ + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2e^- \longrightarrow Ni + 6NH_3$	−0.49
$NiO_2 + 4H^+ + 2e^- \longrightarrow Ni^{2+} + 2H_2O$	+1.593
$NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$	+0.49
$NiS + 2e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.957
$NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^-$	+0.10
$Np^{3+} + 3e^- \longrightarrow Np$	−1.856
$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.401
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	+1.69
$PbS + 2e^- \longrightarrow Pb + S^{2-}$	−0.95

Half-Reaction	$E°$ (V)
$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2e^- \longrightarrow Pd + 4Cl^-$	+0.591
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20
$[PtBr_4]^{2-} + 2e^- \longrightarrow Pt + 4Br^-$	+0.58
$[PtCl_4]^{2-} + 2e^- \longrightarrow Pt + 4Cl^-$	+0.755
$[PtCl_6]^{2-} + 2e^- \xrightarrow{PtCl_4^{2-}} + 2Cl^-$	+0.68
$Pu^3 + 3e^- \longrightarrow Pu$	−2.03
$Ra^{2+} + 2e^- \longrightarrow Ra$	−2.92
$Rb^+ + e^- \longrightarrow Rb$	−2.98
$[RhCl_6]^{3-} + 3e^- \longrightarrow Rh + 6Cl^-$	+0.44
$S + 2e^- \longrightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \longrightarrow H_2S$	+0.142
$Sc^{3+} + 3e^- \longrightarrow Sc$	−2.09
$Se + 2H^+ + 2e^- \longrightarrow H_2Se$	−0.399
$[SiF_6]^{2-} + 4e^- \longrightarrow Si + 6F^-$	−1.2
$SiO_3^{2-} + 3H_2O + 4e^- \longrightarrow Si + 6OH^-$	−1.697
$SiO_2 + 4H^+ + 4e^- \longrightarrow Si + 2H_2O$	−0.86
$Sm^{3+} + 3e^- \longrightarrow Sm$	−2.304
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.151
$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.1375
$[SnF_6]^{2-} + 4e^- \longrightarrow Sn + 6F^-$	−0.25
$SnS + 2e^- \longrightarrow Sn + S^{2-}$	−0.94
$Sr^{2+} + 2e^- \longrightarrow Sr$	−2.89
$TeO_2 + 4H^+ + 4e^- \longrightarrow Te + 2H_2O$	+0.593
$Th^{4+} + 4e^- \longrightarrow Th$	−1.90
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.630
$U^{3+} + 3e^- \longrightarrow U$	−1.79
$V^{2+} + 2e^- \longrightarrow V$	−1.19
$Y^{3+} + 3e^- \longrightarrow Y$	−2.37
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.7618
$[Zn(CN)_4]^{2-} + 2e^- \longrightarrow Zn + 4CN^-$	−1.26
$[Zn(NH_3)_4]^{2+} + 2e^- \longrightarrow Zn + 4NH_3$	−1.04

Half-Reaction	$E°$ (V)
$\mathrm{Zn(OH)_2 + 2\,e^- \longrightarrow Zn + 2\,OH^-}$	−1.245
$\mathrm{[Zn(OH)_4]^2 + 2\,e^- \longrightarrow Zn + 4\,OH^-}$	−1.199
$\mathrm{ZnS + 2\,e^- \longrightarrow Zn + S^{2-}}$	−1.40
$\mathrm{Zr^4 + 4\,e^- \longrightarrow Zr}$	−1.539

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6.6: Gibbs Energy and Redox Reactions

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathbf{Co(s)}$ with $\mathbf{Ni^{2+}(aq)}$ to form $\mathbf{Ni(s)}$ and $\mathbf{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathbf{Ni^{2+}}$ by a factor of 100, so that $\mathbf{[Ni^{2+}]}$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Gibbs Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \text{J}}{1\ \text{V}} = 1\ \text{C} = \text{A} \cdot \text{s}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \text{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \text{mol e}^-} \right) \\ &= 9.64833212 \times 10^4\ \text{C/mol e}^- \\ &\simeq 96,485\ J/(\text{V} \cdot \text{mol e}^-) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{6.6.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 6.6.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG° for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E°, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 6.6.1 to calculate ΔG°. If ΔG° is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E°. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E° values:

$$\begin{aligned} \text{cathode (reduction):}\quad & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) && E^\circ_{cathode} = 1.36\ \text{V} \\ \text{anode (oxidation):}\quad & 2Br^-(aq) \rightarrow Br_2(aq) + 2e^- && E^\circ_{anode} = 1.09\ \text{V} \end{aligned}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E° is not affected:

$$\begin{aligned}
\text{cathode} \quad & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) && E^\circ_{cathode} = 1.36\ V \\
\text{anode} \quad & 3Br^-(aq) \rightarrow 3Br_2(aq) + 6e^- && E^\circ_{anode} = 1.09\ V \\
\text{overall} \quad & Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l) && E^\circ_{cell} = 0.27\ V
\end{aligned}$$

B

We can now calculate ΔG° using Equation 6.6.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}
\Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\
&= -(6\ \text{mole})[96,485\ \text{J/(V} \cdot \text{mol)}(0.27\ \text{V})] \\
&= -15.6 \times 10^4\ \text{J} \\
&= -156\ \text{kJ/mol}\ Cr_2O_7^{2-}
\end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

? Exercise 6.6.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \longrightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $Fe^{3+}(aq)$ to $Fe(s)$ is not listed in the table, but two related reductions are given:

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \quad E^\circ = +0.77V$$

$$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s) \quad E^\circ = -0.45V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o(= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

\begin{align*}\ce{Fe^{3+}(aq)} + \ce{e^-} &\rightarrow \ce\mathrm{Fe^{2+}(aq)} &\quad \Delta G^\circ &=-(1)(F)(\textrm{0.77 V})\\[4pt] \ce{Fe^{2+}(aq)}+\ce{2e^-} &\rightarrow\ce{Fe(s)} &\quad\Delta G^\circ &=-(2)(F)(-\textrm{0.45 V})\\[4pt] \ce{Fe^{3+}(aq)}

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 6.6.1 and solving for E^o gives the following:

$$\begin{aligned}
\Delta G^\circ &= -nFE^\circ_{cell} \\
F(0.13\ \text{V}) &= -(3)(F)(E^\circ_{cell}) \\
E^\circ &= -\frac{0.13\ \text{V}}{3} = -0.043\ \text{V}
\end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG^o and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

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

Given the relationship between the standard free-energy change and the standard cell potential (Equation 6.6.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{cell} = \left(\frac{RT}{nF}\right) \ln K \tag{6.6.2}$$

For $T = 298\ K$, Equation 6.6.2 can be simplified as follows:

$$\begin{aligned}
E^\circ_{cell} &= \left(\frac{RT}{nF}\right) \ln K \\
&= \left[\frac{[8.314\ \text{J/(mol} \cdot \text{K)(298 K)}]}{n[96,485\ \text{J/(V} \cdot \text{mol)}]}\right] 2.303 \log K \\
&= \left(\frac{0.0592\ \text{V}}{n}\right) \log K
\end{aligned} \tag{6.6.3}$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 6.6.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Use Equation 6.6.3 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

$$\begin{array}{lll} \text{cathode} & PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) & E^\circ_{cathode} = 1.69\ V \\ \text{anode} & Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- & E^\circ_{anode} = -0.36\ V \\ \text{overall} & Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) & E^\circ_{cell} = 2.05\ V \end{array}$$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 6.6.3 for log K and inserting the values of n and E°,

$$\log K = \frac{nE^\circ}{0.0591\ V} = \frac{2(2.05\ V)}{0.0591\ V} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 6.6.2

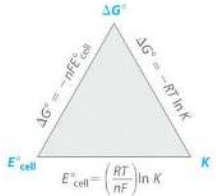
Use the data in Table P2 to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}(aq) + O_2(g) + 4H^+(aq) \rightleftharpoons 2Sn^{4+}(aq) + 2H_2O(l)$$

Answer

5.7×10^{72}

Figure 6.6.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G^\circ < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



ΔG°	E°_{cell}	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 6.6.1: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and E°_{cell}. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and E°_{cell} and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, E°_{cell} and K are also related. Large equilibrium constants correspond to large positive values of E°.

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6.7: Cell Potential Under Nonstandard Conditions

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^{\circ} + RT \ln Q \tag{6.7.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^{o} = -nFE^{o}_{cell}$ (under standard conditions). Substituting these expressions into Equation 6.7.1, we obtain

$$-nFE_{cell} = -nFE^{o}_{cell} + RT \ln Q \tag{6.7.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{6.7.3}$$

Equation 6.7.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 6.7.3 reduces to Equation 6.7.4 and 6.7.5 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{6.7.4}$$

since

$$E^{\circ}_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{6.7.5}$$

Substituting the values of the constants into Equation 6.7.3 with $T = 298\ K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{6.7.6}$$

The Power of the Nernst Equation

The Nernst Equation (6.7.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 6.7.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 6.7.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 6.7.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2\,Ce^{4+}(aq) + 2\,Cl^-(aq) \longrightarrow 2\,Ce^{3+}(aq) + Cl_2(g) \qquad E^\circ_{cell} = 0.25\ V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}]$ = 0.013 M, $[Ce^{3+}]$ = 0.60 M, $[Cl^-]$ = 0.0030 M, P_{Cl_2} = 1.0 atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 6.7.6 instead of Equation 6.7.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^- \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 6.7.6,

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[Ce^{3+}]^2 P_{Cl_2}}{[Ce^{4+}]^2[Cl^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture

Exercise 6.7.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,MnO_2(s) + 3\,O_2(g) + 4\,OH^-(aq) \longrightarrow 4\,MnO_4^-(aq) + 2\,H_2O(l) \quad E^\circ_{cell} = -0.20\ V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2} = 0.20 atm, $[MNO_4^-]$ = 1.0×10^{-4} M, and T = 25°C.

Answer

E_{cell} = −0.22 V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E^\circ cell = 1.10V \tag{6.7.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 6.7.6:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \tag{6.7.8}$$

$$= 1.10\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{1.0\times10^{-6}}{1.0}\right) = 1.28\ \text{V} \tag{6.7.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, [Zn^{2+}] in the anode compartment increases as the zinc electrode dissolves, while [Cu^{2+}] in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio Q = [Zn^{2+}]/[Cu^{2+}] steadily increases, and the cell voltage therefore steadily decreases. Eventually, [Zn^{2+}] = [Cu^{2+}], so Q = 1 and E_{cell} = $E°_{cell}$. Beyond this point, [Zn^{2+}] will continue to increase in the anode compartment, and [Cu^{2+}] will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0 × 10^{-6} M Cu^{2+}), Q = 1.0 × 10^6, and the cell potential will be reduced to 0.92 V.

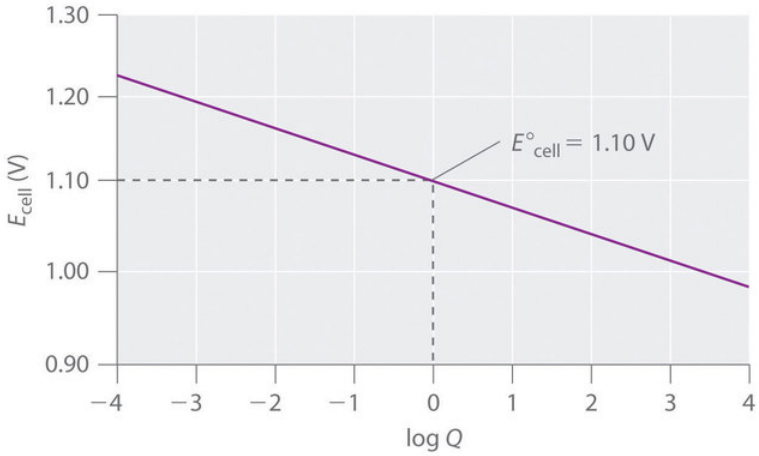


Figure 6.7.1: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When [Zn^{2+}] = [Cu^{2+}], log Q = 0 and E_{cell} = $E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure 6.7.1. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when E_{cell} = 0 is calculated as follows:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q = 0 \tag{6.7.10}$$

$$E^\circ = \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \tag{6.7.11}$$

$$\log Q = \frac{E^\circ n}{0.0591\ \text{V}} = \frac{(1.10\ \text{V})(2)}{0.0591\ \text{V}} = 37.23 \tag{6.7.12}$$

$$Q = 10^{37.23} = 1.7\times10^{37} \tag{6.7.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7 × 10^{37} at 25°C.



The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)} \,|\, \mathrm{Ag^+}(aq, 0.010\ M) \,||\, \mathrm{Ag^+}(aq, 1.0\ M) \,|\, \mathrm{Ag(s)} \tag{6.7.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag(s)} \tag{6.7.15}$$

anode:

$$\mathrm{Ag(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{6.7.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{6.7.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right) \log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

✔ Example 6.7.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.

B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$Mn^{2+}(aq, 2.0\ M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\ M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 6.7.6:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \\ &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ \text{V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 6.7.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

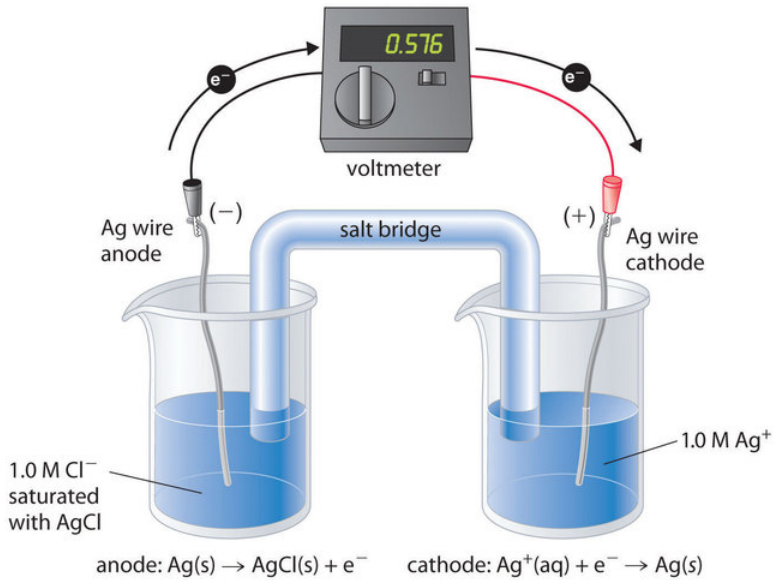


Figure 6.7.1: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 6.7.1, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [Ag^+][Cl^-].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting:

$$\begin{aligned}[Ag^+] &= \frac{K_{sp}}{[Cl^-]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$Ag^+(aq, \text{concentrated}) \rightarrow Ag^+(aq, \text{dilute})$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{\text{cell}} &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{1}\right) \log\left(\frac{[Ag^+]_{\text{dilute}}}{[Ag^+]_{\text{concentrated}}}\right) \\ &= -0.0591\ \text{V}\ \log\left(\frac{K_{\text{sp}}}{1.0}\right) \\ &= -0.0591\ \text{V}\ \log K_{\text{sp}} \qquad (6.7.18)\end{aligned}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 6.7.18 for K_{sp},

$$\begin{aligned}\log K_{\text{sp}} &= \frac{-E_{\text{cell}}}{0.0591\ \text{V}} = \frac{-0.580\ \text{V}}{0.0591\ \text{V}} = -9.81 \\ K_{\text{sp}} &= 1.5 \times 10^{-10}\end{aligned}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 6.7.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 6.7.1, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ M} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, concentrated) \rightarrow Pb^{2+}(aq, dilute)$$

so

$$E_{cell} = E^{\circ}_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$

$$0.230\ V = 0\ V - \left(\frac{0.0591\ V}{2}\right) \log\left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V \log\left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = \log K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise 6.7.3

A concentration cell similar to the one described in Example 6.7.3 contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 6.7.3, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

Example 6.7.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$Zn(s)|Zn^{2+}(aq, 1.0\ M)||H^+(aq, ?\ M)|H_2(g, 1.0\ atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 6.7.6), we can calculate $[H^+]$ under nonstandard conditions:

$$\begin{aligned} E_{cell} &= E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right)\log\left(\frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}\right) \\ 0.26\ V &= 0.76\ V - \left(\frac{0.0591\ V}{2}\right)\log\left(\frac{(1.0)(1.0)}{[H^+]^2}\right) \\ 16.9 &= \log\left(\frac{1}{[H^+]^2}\right) = \log[H^+]^{-2} = (-2)\log[H^+] \\ 8.46 &= -\log[H^+] \\ 8.5 &= pH \end{aligned}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 6.7.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)} \mid Pb^{2+}(aq, ?M) \parallel H^+(aq), 1.0M \mid O_2(g, 1.0atm) \mid Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical

except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

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6.8: Corrosion

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathbf{Fe_2O_3 \cdot \mathit{x}\, H_2O}$), commonly known as rust, that does not provide a tight protective film (Figure **6.8.1**). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

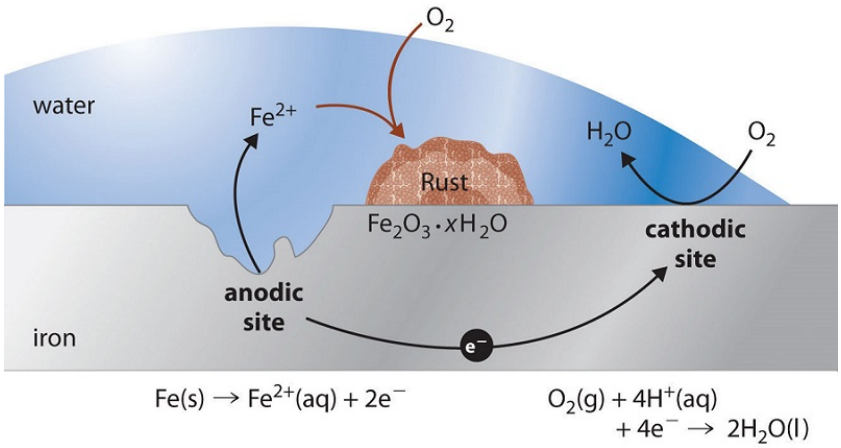


Figure **6.8.1**: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust (Fe_2O_3•xH_2O) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathbf{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(l)}$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$\mathrm{Fe\,(s) \longrightarrow Fe^{2+}\,(aq) + 2\,e^-}$$

with $E^o_{SRP} = -0.45\ V$.

- overall:

$$\mathrm{2\,Fe\,(s) + O_2\,(g) + 4\,H^+\,(aq) \longrightarrow 2\,Fe^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{6.8.1}$$

with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3+}}$, as represented in the following equation:

$$\mathrm{4\,Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4\,x)H_2O \ \rightarrow 2\,Fe_2O_3 \ \cdot x\,H_2O + 4\,H^+\,(aq)} \tag{6.8.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 6.8.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 6.8.2).

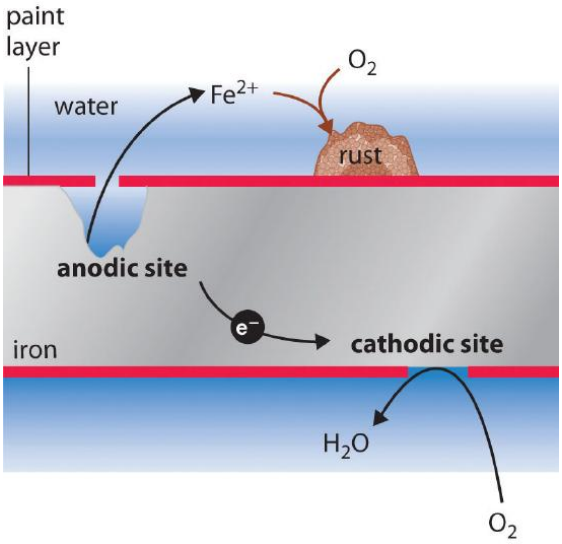


Figure 6.8.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

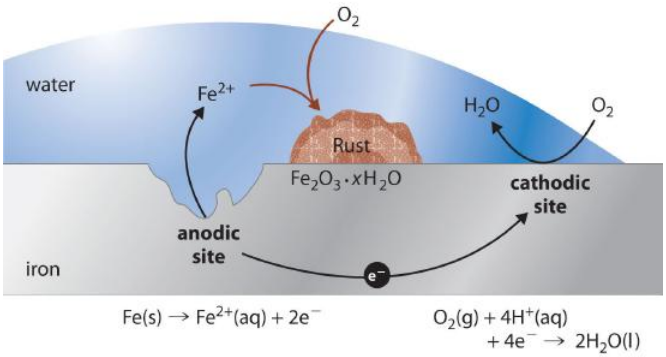


Figure 6.8.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for $\mathbf{Sn^{2+}}$ ($E° = -0.14$ V) and Fe^{2+} ($E° = -0.45$ V) in Table P2 show that **Fe** is more easily oxidized than **Sn**. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 6.8.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as **Zn** ($E° = -0.76$ V for $\mathbf{Zn^{2+} + 2\,e^- \longrightarrow Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{6.8.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{6.8.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{6.8.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 6.8.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

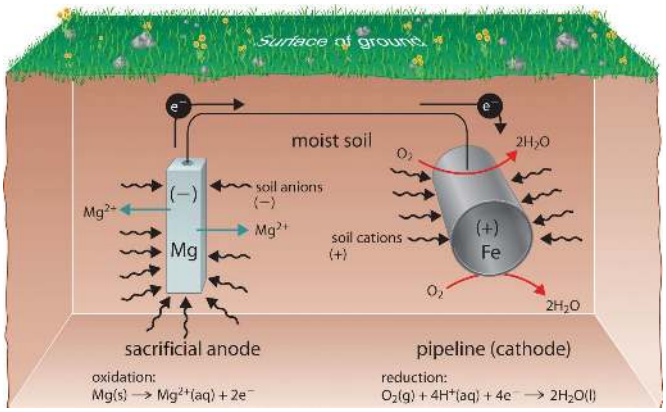


Figure **6.8.4**: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 6.8.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°°_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°°_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°°_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E°°_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

cathode:	$O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$E°_{cathode} = 1.23\ V$
anode:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$E°_{anode} = -0.45\ V$
overall:	$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$E°_{overall} = 1.68\ V$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 6.8.5).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 6.8.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the **Cu/Fe** pipe joints will lead to rapid corrosion.

Answer b

Any existing **Pb/Fe** joints should be examined carefully for corrosion of the iron pipes due to the **Pb—Fe** junction; the less active **Pb** will have served as the cathode for the reduction of O_2, promoting oxidation of the more active **Fe** nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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6.9: Electrolysis

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a 1 $M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure 6.9.1*a*).

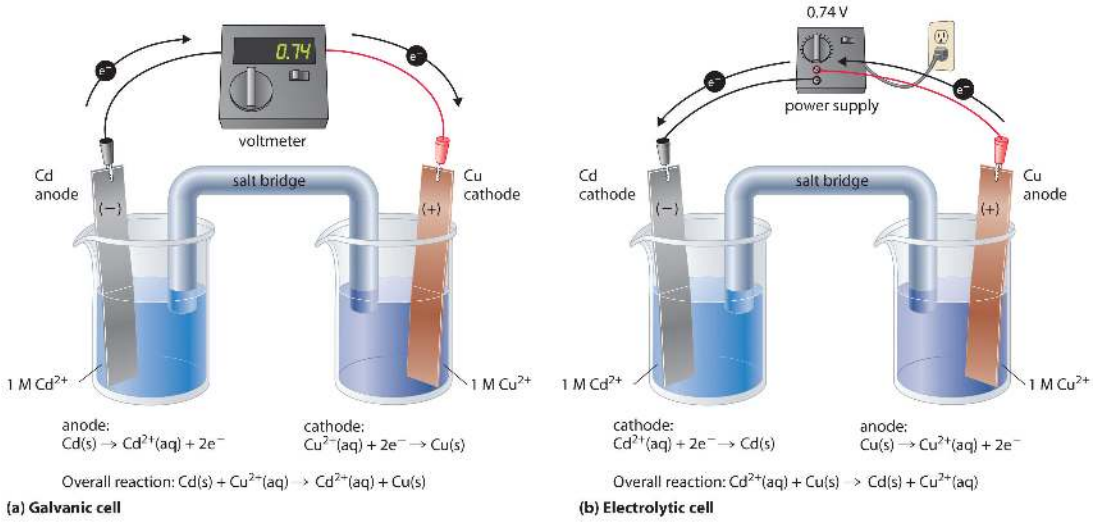


Figure 6.9.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)}$$

with $E^{\circ}_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^{o} < 0$):

$$\begin{aligned}\Delta G^{\circ} &= -nFE^{\circ}_{\text{cell}} \\ &= -(2\ \text{mol e}^{-})[96,485\ \text{J}/(\text{V}\cdot\text{mol})](0.74\ \text{V}) \\ &= -140\ \text{kJ (per mole Cd)}\end{aligned}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure 6.9.1*b*). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{6.9.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{6.9.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{6.9.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 6.9.1.

Table 6.9.1: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{6.9.4}$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a Downs cell (Figure 6.9.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

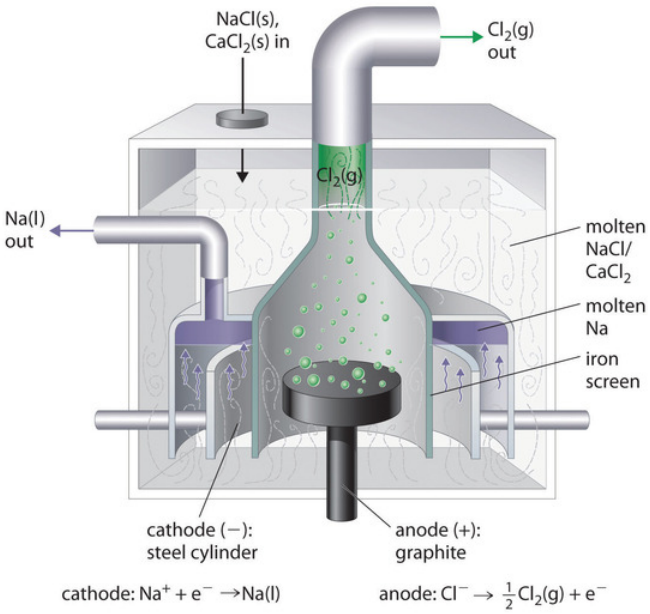


Figure 6.9.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,Al_2O_3(l) + 3\,C(s) \longrightarrow 4\,Al(l) + 3\,CO_2(g) \tag{6.9.5}$$

Oxide ions react with oxidized carbon at the anode, producing $CO_2(g)$.

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

✔ Example 6.9.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 6.9.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 6.9.3).

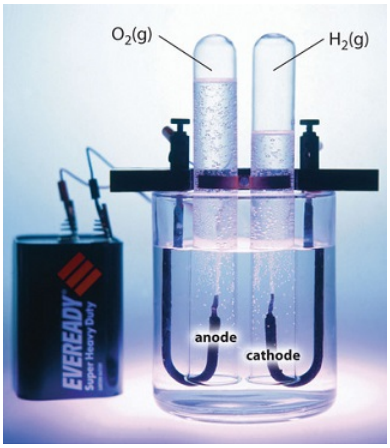


Figure 6.9.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{6.9.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{6.9.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{6.9.8}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{O_2}P_{H_2}^2) \tag{6.9.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{6.9.10}$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 6.9.4.

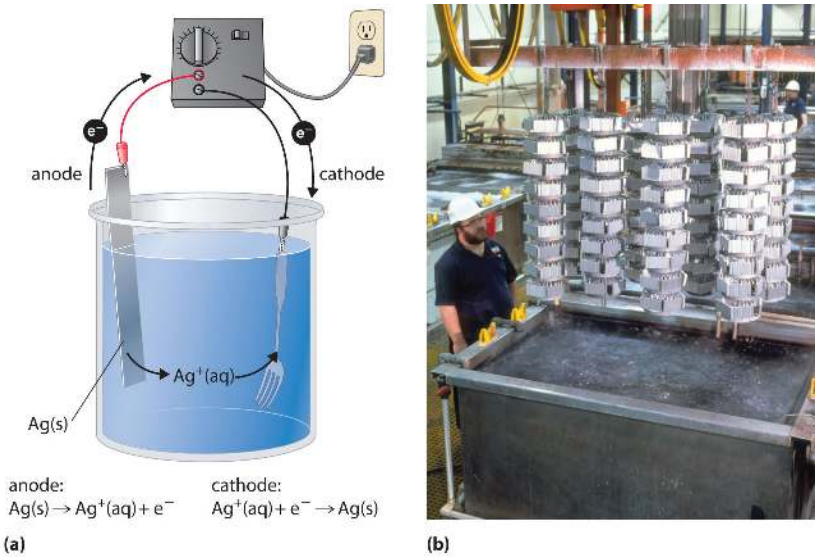


Figure 6.9.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E^\circ_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq) + e^-} \qquad E^\circ_{anode} = 0.80V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E^o_{cell} = 0\,V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$$

1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2+}}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{6.9.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\text{ A})(6.0\text{ min})(60\text{ s/min}) \\ &= 220\text{ A}\cdot\text{s} \\ &= 220\text{ C} \end{aligned}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2+}}$ is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\text{ C}}{96{,}485\text{ C/mol}} \\ &= 2.3 \times 10^{-3}\text{ mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 6.9.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.
B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}485\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned}\text{amperes} &= \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \\ &= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A}\end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise 6.9.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h



Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

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Index

A

absolute enthalpy
6.4: Cell Potential Under Standard Conditions
absolute free energy
6.4: Cell Potential Under Standard Conditions
absolute zero
2.3: The Molecular Interpretation of Entropy
acid ionization
5.2: Brønsted–Lowry Acids and Bases
acid ionization constant
5.6: Strong Acids and Bases
acidic
5.5: The pH Scale
activity
4.4: Free Energy and the Equilibrium Constant
ampere (unit)
6.6: Gibbs Energy and Redox Reactions
amphiprotic
5.2: Brønsted–Lowry Acids and Bases
5.4: The Autoionization of Water
amphoteric
5.2: Brønsted–Lowry Acids and Bases
anode
6.3: Voltaic Cells
Arrhenius acid
5.1: Acids and Bases - A Brief Review
Arrhenius base
5.1: Acids and Bases - A Brief Review
Arrhenius equation
3.11: Arrhenius Equation
autoionization
5.2: Brønsted–Lowry Acids and Bases
average rate
3.1: Chemical Reaction Rates

B

Balancing Redox Equations
6.2: Balanced Oxidation-Reduction Equations
base ionization
5.2: Brønsted–Lowry Acids and Bases
base ionization constant
5.6: Strong Acids and Bases
basic
5.5: The pH Scale
bimolecular reaction
3.9: Reaction Mechanisms
buffer
5.14: Buffered Solutions
buffer capacity
5.14: Buffered Solutions
buret
5.15: Acid-Base Titrations

C

catalyst
3.2: Factors Affecting Reaction Rates
cathode
6.3: Voltaic Cells
cell potential
6.3: Voltaic Cells
collision theory
3.10: The Collision Theory
combination reaction
6.1: Oxidation States and Redox Reactions
common ion effect
4.6: Precipitation and Dissolution
5.13: The Common-Ion Effect
concentration cell
6.7: Cell Potential Under Nonstandard Conditions
conjugate acid
5.2: Brønsted–Lowry Acids and Bases
conjugate base
5.2: Brønsted–Lowry Acids and Bases
corrosion
6.8: Corrosion
coulomb (unit)
6.6: Gibbs Energy and Redox Reactions

D

decomposition reaction
6.1: Oxidation States and Redox Reactions
disproportionation reaction
6.1: Oxidation States and Redox Reactions

E

electrochemical cell
6.3: Voltaic Cells
electrode
6.3: Voltaic Cells
electrolysis
6.9: Electrolysis
electrolytic cell
6.3: Voltaic Cells
6.9: Electrolysis
electroplating
6.9: Electrolysis
elementary reaction
3.9: Reaction Mechanisms
entropy
2.2: Entropy and the Second Law of Thermodynamics
equilibrium
4.2: Chemical Equilibria
equilibrium constant
4.3: Equilibrium Constants
4.4: Free Energy and the Equilibrium Constant
equivalence point
5.15: Acid-Base Titrations

F

faraday (unit)
6.6: Gibbs Energy and Redox Reactions
fugacity
4.4: Free Energy and the Equilibrium Constant

G

galvanic cell
6.3: Voltaic Cells
glass electrode
6.4: Cell Potential Under Standard Conditions

H

Hall–Héroult cell
6.9: Electrolysis
heterogeneous equilibria
4.3: Equilibrium Constants
homogeneous equilibria
4.3: Equilibrium Constants
hydrolysis reaction
5.12: Acid-Base Properties of Salt Solutions
hydronium ion
5.1: Acids and Bases - A Brief Review

I

indicator electrode
6.4: Cell Potential Under Standard Conditions
initial rate
3.1: Chemical Reaction Rates
instantaneous rate
3.1: Chemical Reaction Rates
integrated rate law
3.4: Integrated Rate Laws
intermediate
3.9: Reaction Mechanisms
internal energy
2.2: Entropy and the Second Law of Thermodynamics
irreversible process
2.2: Entropy and the Second Law of Thermodynamics

J

junction potential
6.3: Voltaic Cells

K

Kc
4.3: Equilibrium Constants
Kp
4.3: Equilibrium Constants

L

Law of Mass Action
4.3: Equilibrium Constants
Le Chatelier's principle
4.8: Shifting Equilibria - Le Chatelier’s Principle
Leveling Effect
5.6: Strong Acids and Bases
Lewis acid
5.3: Lewis Acids and Bases
Lewis base
5.3: Lewis Acids and Bases

M

Method of Initial Rates
3.3: Rate Laws
molar solubility
4.6: Precipitation and Dissolution
molecularity
3.9: Reaction Mechanisms

N

Nernst equation
6.7: Cell Potential Under Nonstandard Conditions
neutral
5.5: The pH Scale
nonspontaneous process
6.9: Electrolysis

O

overall reaction order
3.3: Rate Laws
overvoltage
6.9: Electrolysis
oxidant
6.3: Voltaic Cells
oxidation number
6.1: Oxidation States and Redox Reactions
oxidation state method
6.2: Balanced Oxidation-Reduction Equations
oxidizing agent
6.1: Oxidation States and Redox Reactions
oxyacid
5.7: Weak Acids

P

percent ionization
5.7: Weak Acids
pH
5.5: The pH Scale
pOH
5.5: The pH Scale
position of equilibrium
4.8: Shifting Equilibria - Le Chatelier's Principle
Prophylactic Protection
6.8: Corrosion

R

rate constant
3.3: Rate Laws
rate expression
3.1: Chemical Reaction Rates
rate law
3.3: Rate Laws
rate of reaction
3.1: Chemical Reaction Rates
reaction mechanism
3.9: Reaction Mechanisms
reaction order
3.3: Rate Laws
reaction quotient
4.3: Equilibrium Constants
6.7: Cell Potential Under Nonstandard Conditions
redox reaction
6.1: Oxidation States and Redox Reactions
reducing agent
6.1: Oxidation States and Redox Reactions
reductant
6.3: Voltaic Cells
reference electrode
6.4: Cell Potential Under Standard Conditions
Reversible Process
2.2: Entropy and the Second Law of Thermodynamics
reversible reaction
4.2: Chemical Equilibria

S

sacrificial anode
6.8: Corrosion
sacrificial electrode
6.8: Corrosion
salt
5.12: Acid-Base Properties of Salt Solutions
salt bridge
6.3: Voltaic Cells
salt solution
5.12: Acid-Base Properties of Salt Solutions
saturated calomel electrode
6.4: Cell Potential Under Standard Conditions
second law of thermodynamics
2.2: Entropy and the Second Law of Thermodynamics
2.3: The Molecular Interpretation of Entropy
selective precipitation
4.6: Precipitation and Dissolution
single replacement reaction
6.1: Oxidation States and Redox Reactions
solubility product
4.6: Precipitation and Dissolution
5.13: The Common-Ion Effect
solvation
2.3: The Molecular Interpretation of Entropy
spectator ion
5.14: Buffered Solutions
standard cell potential
6.4: Cell Potential Under Standard Conditions
standard electrode potential
6.4: Cell Potential Under Standard Conditions
standard hydrogen electrode
6.4: Cell Potential Under Standard Conditions
standard molar entropy
2.4: Entropy Changes in Chemical Reactions
stress
4.8: Shifting Equilibria - Le Chatelier's Principle
strong acid
5.6: Strong Acids and Bases
strong base
5.6: Strong Acids and Bases

T

termolecular reaction
3.9: Reaction Mechanisms
Third Law of Thermodynamics
2.3: The Molecular Interpretation of Entropy
titrant
5.15: Acid-Base Titrations
titration
5.15: Acid-Base Titrations

U

unimolecular reaction
3.9: Reaction Mechanisms

V

voltaic cell
6.3: Voltaic Cells

W

water gas shift reaction
4.3: Equilibrium Constants
weak acid
5.7: Weak Acids
weak base
5.9: Weak Bases

Glossary

Sample Word 1 | Sample Definition 1

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    - 2.6: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
  - 3: Reaction Kinetics - *Undeclared*
    - 3.1: Chemical Reaction Rates - *CC BY 4.0*
    - 3.2: Factors Affecting Reaction Rates - *CC BY 4.0*
    - 3.3: Rate Laws - *CC BY 4.0*
    - 3.4: Integrated Rate Laws - *CC BY 4.0*
    - 3.5: First-Order Reactions - *Undeclared*
    - 3.6: Second-Order Reactions - *Undeclared*
    - 3.7: Zero-Order Reactions - *Undeclared*
    - 3.8: Pseudo-1st-order reactions - *Undeclared*
    - 3.9: Reaction Mechanisms - *CC BY 4.0*
    - 3.10: The Collision Theory - *CC BY-NC-SA 4.0*
    - 3.11: Arrhenius Equation - *CC BY 4.0*
    - 3.12: Kinetics of Catalysis - *CC BY-NC-SA 4.0*
  - 4: Chemical Equilibrium - *Undeclared*
    - 4.1: Prelude to Equilibrium - *CC BY 4.0*
    - 4.2: Chemical Equilibria - *CC BY 4.0*
    - 4.3: Equilibrium Constants - *CC BY 4.0*
    - 4.4: Free Energy and the Equilibrium Constant - *CC BY-NC-SA 3.0*
    - 4.5: Equilibrium Calculations - *CC BY 4.0*
    - 4.6: Precipitation and Dissolution - *CC BY 4.0*
    - 4.7: Solubility Products - *CC BY 4.0*
    - 4.8: Shifting Equilibria - Le Chatelier's Principle - *CC BY 4.0*
  - 5: Acids and Bases - *Undeclared*
    - 5.1: Acids and Bases - A Brief Review - *CC BY-NC-SA 3.0*
    - 5.2: Brønsted–Lowry Acids and Bases - *CC BY-NC-SA 3.0*
    - 5.3: Lewis Acids and Bases - *CC BY-NC-SA 3.0*
    - 5.4: The Autoionization of Water - *CC BY-NC-SA 3.0*
    - 5.5: The pH Scale - *CC BY-NC-SA 3.0*
    - 5.6: Strong Acids and Bases - *CC BY-NC-SA 3.0*
    - 5.7: Weak Acids - *CC BY-NC-SA 3.0*
    - 5.8: Ionization Constants of Weak Acids - *CC BY 4.0*
    - 5.9: Weak Bases - *CC BY-NC-SA 3.0*
    - 5.10: Ionization Constants of Weak Bases - *CC BY 4.0*
    - 5.11: Relationship Between Ka and Kb - *CC BY-NC-SA 3.0*

- 5.12: Acid-Base Properties of Salt Solutions - *CC BY-NC-SA 3.0*
- 5.13: The Common-Ion Effect - *CC BY-NC-SA 3.0*
- 5.14: Buffered Solutions - *CC BY-NC-SA 3.0*
- 5.15: Acid-Base Titrations - *CC BY-NC-SA 3.0*

- 6: Electrochemistry - *Undeclared*
  - 6.1: Oxidation States and Redox Reactions - *CC BY-NC-SA 3.0*
  - 6.2: Balanced Oxidation-Reduction Equations - *CC BY-NC-SA 3.0*
  - 6.3: Voltaic Cells - *CC BY-NC-SA 3.0*
  - 6.4: Cell Potential Under Standard Conditions - *CC BY-NC-SA 3.0*
  - 6.5: Standard Electrode (Half-Cell) Potentials - *CC BY 4.0*
  - 6.6: Gibbs Energy and Redox Reactions - *CC BY-NC-SA 3.0*
  - 6.7: Cell Potential Under Nonstandard Conditions - *CC BY-NC-SA 3.0*
  - 6.8: Corrosion - *CC BY-NC-SA 3.0*
  - 6.9: Electrolysis - *CC BY-NC-SA 3.0*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*
  - Detailed Licensing - *Undeclared*

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- AUCHE 112 - General Chemistry II (Elizabeth McGinitie) - *Undeclared*
  - Front Matter - *Undeclared*
    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Thermochemistry - *Undeclared*
    - 1.1: The Nature of Energy - *CC BY-NC-SA 4.0*
    - 1.2: Energy Basics - *CC BY 4.0*
    - 1.3: Calorimetry - *CC BY 4.0*
    - 1.4: Enthalpy - *CC BY 4.0*
    - 1.5: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
    - 1.6: Bond Energies - *CC BY-NC-SA 4.0*
  - 2: Spontaneity, Entropy and Free Energy - *Undeclared*
    - 2.1: Spontaneity - *CC BY 4.0*
    - 2.2: Entropy and the Second Law of Thermodynamics - *CC BY-NC-SA 3.0*
    - 2.3: The Molecular Interpretation of Entropy - *CC BY-NC-SA 3.0*
    - 2.4: Entropy Changes in Chemical Reactions - *CC BY-NC-SA 3.0*
    - 2.5: Gibbs Energy - *CC BY 4.0*
    - 2.6: Standard Thermodynamic Properties for Selected Substances - *CC BY 4.0*
  - 3: Reaction Kinetics - *Undeclared*
    - 3.1: Chemical Reaction Rates - *CC BY 4.0*
    - 3.2: Factors Affecting Reaction Rates - *CC BY 4.0*
    - 3.3: Rate Laws - *CC BY 4.0*
    - 3.4: Integrated Rate Laws - *CC BY 4.0*
    - 3.5: First-Order Reactions - *Undeclared*
    - 3.6: Second-Order Reactions - *Undeclared*
    - 3.7: Zero-Order Reactions - *Undeclared*
    - 3.8: Pseudo-1st-order reactions - *Undeclared*
    - 3.9: Reaction Mechanisms - *CC BY 4.0*
    - 3.10: The Collision Theory - *CC BY-NC-SA 4.0*
    - 3.11: Arrhenius Equation - *CC BY 4.0*
    - 3.12: Kinetics of Catalysis - *CC BY-NC-SA 4.0*
  - 4: Chemical Equilibrium - *Undeclared*
    - 4.1: Prelude to Equilibrium - *CC BY 4.0*
    - 4.2: Chemical Equilibria - *CC BY 4.0*
    - 4.3: Equilibrium Constants - *CC BY 4.0*
    - 4.4: Free Energy and the Equilibrium Constant - *CC BY-NC-SA 3.0*
    - 4.5: Equilibrium Calculations - *CC BY 4.0*
    - 4.6: Precipitation and Dissolution - *CC BY 4.0*
    - 4.7: Solubility Products - *CC BY 4.0*
    - 4.8: Shifting Equilibria - Le Chatelier's Principle - *CC BY 4.0*
  - 5: Acids and Bases - *Undeclared*
    - 5.1: Acids and Bases - A Brief Review - *CC BY-NC-SA 3.0*
    - 5.2: Brønsted–Lowry Acids and Bases - *CC BY-NC-SA 3.0*
    - 5.3: Lewis Acids and Bases - *CC BY-NC-SA 3.0*
    - 5.4: The Autoionization of Water - *CC BY-NC-SA 3.0*
    - 5.5: The pH Scale - *CC BY-NC-SA 3.0*
    - 5.6: Strong Acids and Bases - *CC BY-NC-SA 3.0*
    - 5.7: Weak Acids - *CC BY-NC-SA 3.0*
    - 5.8: Ionization Constants of Weak Acids - *CC BY 4.0*
    - 5.9: Weak Bases - *CC BY-NC-SA 3.0*
    - 5.10: Ionization Constants of Weak Bases - *CC BY 4.0*
    - 5.11: Relationship Between Ka and Kb - *CC BY-NC-SA 3.0*

- 5.12: Acid-Base Properties of Salt Solutions - *CC BY-NC-SA 3.0*
- 5.13: The Common-Ion Effect - *CC BY-NC-SA 3.0*
- 5.14: Buffered Solutions - *CC BY-NC-SA 3.0*
- 5.15: Acid-Base Titrations - *CC BY-NC-SA 3.0*

- 6: Electrochemistry - *Undeclared*
  - 6.1: Oxidation States and Redox Reactions - *CC BY-NC-SA 3.0*
  - 6.2: Balanced Oxidation-Reduction Equations - *CC BY-NC-SA 3.0*
  - 6.3: Voltaic Cells - *CC BY-NC-SA 3.0*
  - 6.4: Cell Potential Under Standard Conditions - *CC BY-NC-SA 3.0*
  - 6.5: Standard Electrode (Half-Cell) Potentials - *CC BY 4.0*
  - 6.6: Gibbs Energy and Redox Reactions - *CC BY-NC-SA 3.0*
  - 6.7: Cell Potential Under Nonstandard Conditions - *CC BY-NC-SA 3.0*
  - 6.8: Corrosion - *CC BY-NC-SA 3.0*
  - 6.9: Electrolysis - *CC BY-NC-SA 3.0*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
  - Detailed Licensing - *Undeclared*
  - Detailed Licensing - *Undeclared*