NASSAU COMMUNITY COLLEGE CHE152 - GENERAL CHEMISTRY II



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CHE152 - General Chemistry II

Dr. Rakhi Agarwal

Spring 2020- Fall 2020

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This text was compiled on 01/12/2026

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Licensing

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CHAPTER OVERVIEW

1: Kinetics

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General Chemistry

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

1.1: Prelude to Kinetics
1.2: Chemical Reaction Rates
1.3: Factors Affecting Reaction Rates
1.4: Rate Laws
1.5: Integrated Rate Laws
1.6: Collision Theory
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1.E: Kinetics (Exercises)

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1.1: Prelude to Kinetics

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.



Figure **1.1.1**: *An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.*

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. In this chapter, we will examine the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to determine and describe the rate at which reactions occur.

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1.2: 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 **1.2.1** 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 **1.2.1**: 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 **1.2.2**). 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.

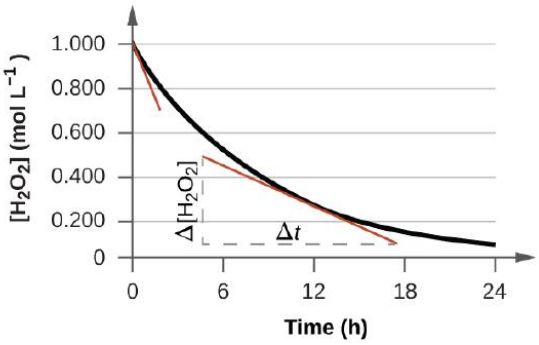


Figure **1.2.1**: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" 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 **1.2.2**). 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:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2 \qquad (1.2.1)$$

$$2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2 \tag{1.2.2}$$

Equation 1.2.1 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 1.2.2), 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.

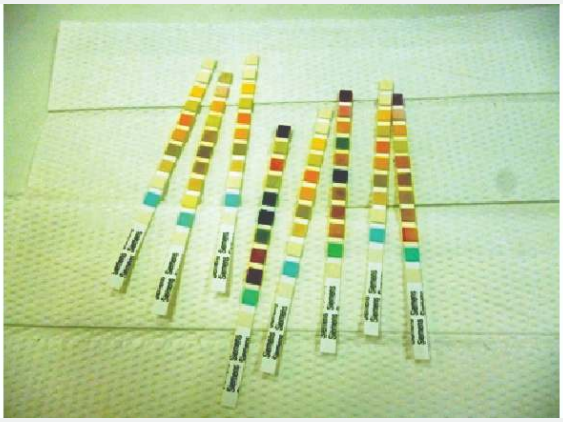


Figure 1.2.2: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

Relative Rates of Reaction

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

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

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:

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

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

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

Figure 1.2.3 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:

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

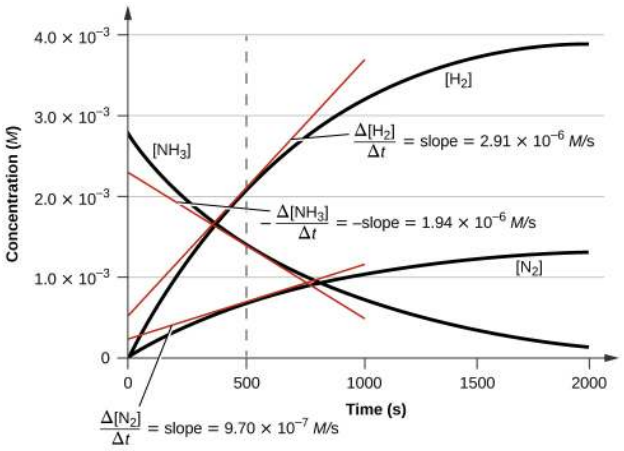


Figure 1.2.3: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,NH_3 \longrightarrow N_2 + 3\,H_2$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

Example 1.2.1: 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 1.2.1

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 1.2.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure **1.2.3** 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 1.2.2

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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1.3: 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.

The Chemical Nature of the Reacting Substances

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

The 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 **1.3.1**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure **1.3.1**: (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* 1.3.1**: *The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

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.

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 **1.3.2**). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathbf{SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)}} \tag{1.3.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathbf{CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}} \tag{1.3.2}$$

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.

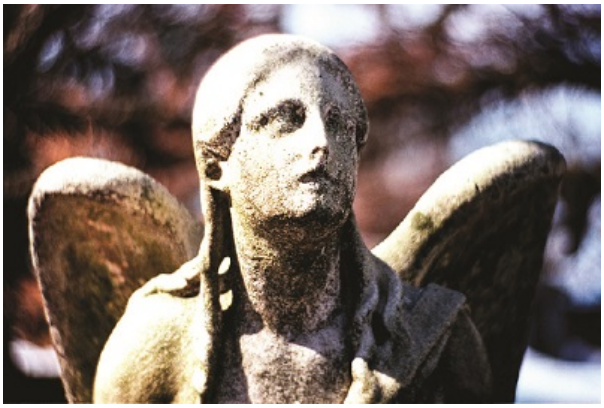


Figure **1.3.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, 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* 1.3.2**: *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

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 **1.3.3**). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

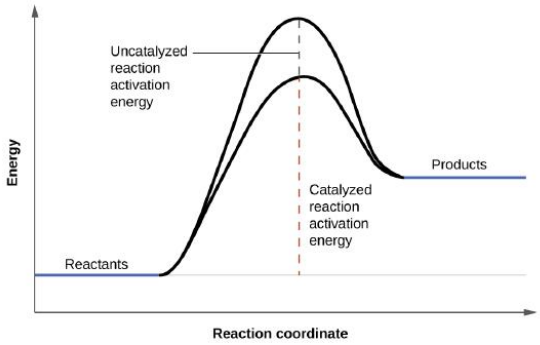


Figure **1.3.3**: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

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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1.4: 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 1.4.1: 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 1.4.1*A*

The rate law for the reaction:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

has been experimentally determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2;
- order in H_2 = 1;
- overall order = 3

? Exercise 1.4.1*B*

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\mathrm{CH_3OH} + \mathrm{CH_3CH_2OCOCH_3} \longrightarrow \mathrm{CH_3OCOCH_3} + \mathrm{CH_3CH_2OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[\mathrm{CH_3OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1;
- order in $CH_3CH_2OCOCH_3$ = 0;
- overall order = 1

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 1.4.2: 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 1.4.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

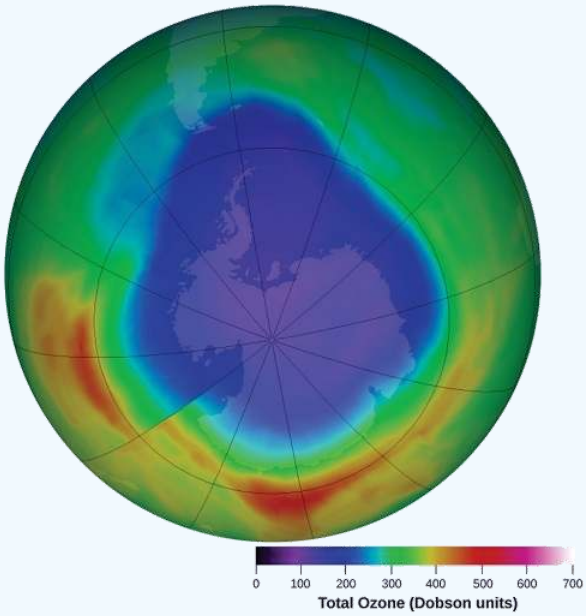


Figure **1.4.1**: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

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	[NO] (mol/L)	$[O_3]$ (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}$ $(\mathrm{mol\,L^{-1}\,s^{-1}})$
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*.

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \cancel{\text{mol L}^{-1}}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \cancel{\text{mol L}^{-1}})(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

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 1.4.2

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

$\text{rate} = k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

✓ Example 1.4.3: 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 **1.4.2**, 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 1.4.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\text{OCl}^-(aq) + \text{I}^-(aq) \longrightarrow \text{OI}^-(aq) + \text{Cl}^-(aq)$$

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:

$$\text{rate} = k[OCl^-]^2[I^-]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

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:

$$NO_2 + CO \longrightarrow NO + CO_2 \quad \text{rate} = k[NO_2]^2$$

$$CH_3CHO \longrightarrow CH_4 + CO \quad \text{rate} = k[CH_3CHO]^2$$

$$2\,N_2O_5 \longrightarrow 2\,NO_2 + O_2 \quad \text{rate} = k[N_2O_5]$$

$$2\,NO_2 + F_2 \longrightarrow 2\,NO_2F \quad \text{rate} = k[NO_2][F_2]$$

$$2\,NO_2Cl \longrightarrow 2\,NO_2 + Cl_2 \quad \text{rate} = k[NO_2Cl]$$

> *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 **1.4.2**, a second-order reaction, we found the units for k to be $\text{L mol}^{-1}\ \text{s}^{-1}$, whereas in Example **1.4.3**, a third order reaction, we found the units for k to be $\text{mol}^{-2}\ \text{L}^2/\text{s}$. More generally speaking, the units for the rate constant for a reaction of order $(m + n)$ are $\text{mol}^{1-(m+n)}\text{L}^{(m+n)-1}\text{s}^{-1}$. Table **1.4.1** summarizes the rate constant units for common reaction orders.

Table **1.4.1**: Rate Constants for Common Reaction Orders

Reaction Order	Units of k
$(m+n)$	$\text{mol}^{1-(m+n)}\text{L}^{(m+n)-1}\text{s}^{-1}$
zero	mol/L/s
first	s^{-1}
second	L/mol/s
third	$mol^{-2}\ L^2\ s^{-1}$

Note that the units in the table can also be expressed in terms of molarity (M) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

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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1.5: 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.

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 1.5.1: 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 1.5.1

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:

$$\ln[A] = (-k)(t) + \ln [A]_0 \tag{1.5.1}$$

$$y = mx + b \tag{1.5.2}$$

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 1.5.2: 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 1.5.1.

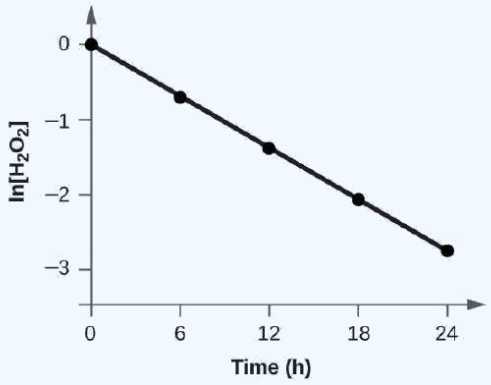


Figure 1.5.1: The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

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 1.5.2

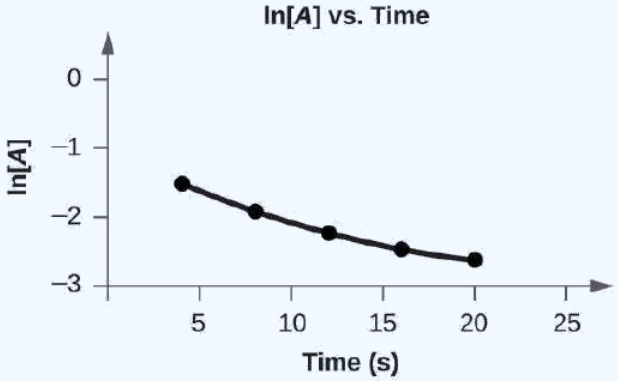
Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

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).

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:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{1.5.3}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 1.5.3: 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 1.5.3

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 1.5.4: 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 **1.5.4**

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 ✔ **1.5.4**

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 **1.5.2**. 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.

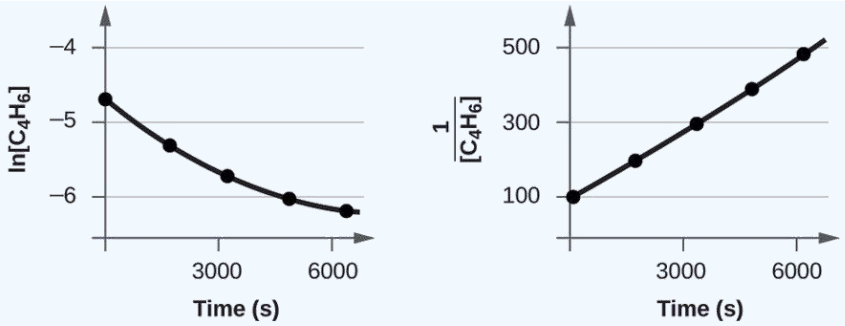


Figure **1.5.2**: These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

? Exercise 1.5.4

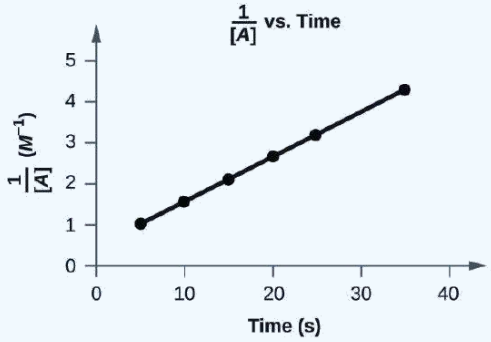
Does the following data fit a second-order rate law?

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).

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 **1.5.3** 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:

$$\text{slope} = -k = 1.3110^{-6}\ \text{mol/L/s}$$

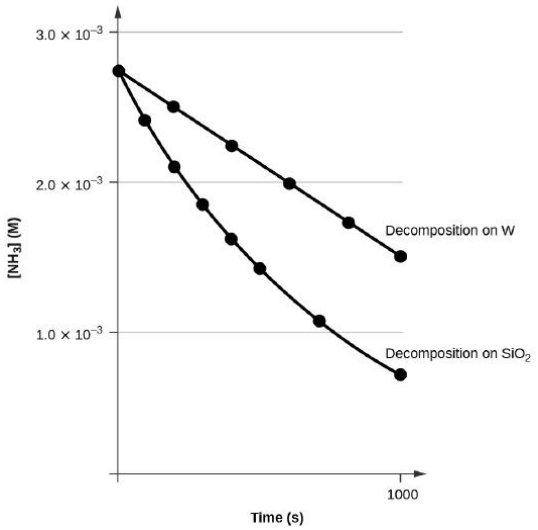


Figure **1.5.3**: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

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.

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 1.5.5: 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 1.5.4.

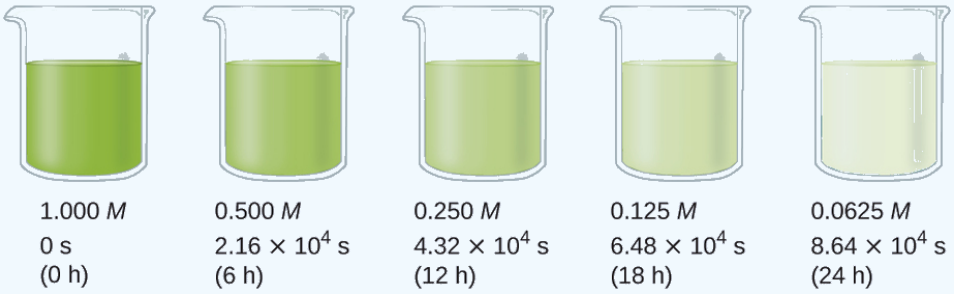


Figure 1.5.4: The decomposition of H_2O_2 ($2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$) *at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.*

Solution The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4\ \text{s}} = 3.21 \times 10^{-5}\ \text{s}^{-1}$$

Exercise 1.5.1

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

Second-Order Reactions

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.

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 **1.5.1**.

Table **1.5.1**: 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.

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 1.5.1):

$$\ln[A] = -kt + \ln[A]_0 \text{ with } t_{1/2} = \frac{0.693}{k}$$

- integrated rate law for second-order reactions (Equation 1.5.3):

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \text{ with } t_{1/2} = \frac{1}{[A]_0 k}$$

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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1.6: Collision Theory

Learning Objectives

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates. Collision theory is based on the following postulates:

Postulates of Collision theory

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\,\text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure **1.6.1**. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (O=C=O). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

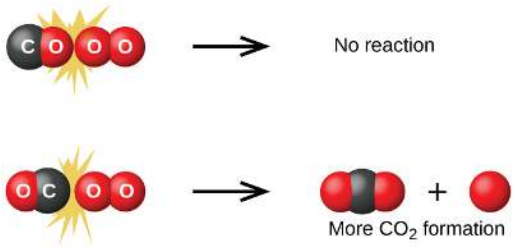


Figure **1.6.1**: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an appropriate activated complex along the way. As Figure **1.6.2** demonstrates, even a collision with the correct orientation can fail to form the reaction product. In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed activated complex or transition state.

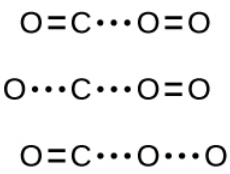


Figure **1.6.2**: Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Figure **1.6.3** shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D:

$$A + B \longrightarrow C + D$$

The figure shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a, the activation energy. Thus, the sum of the kinetic energies of A and B must be **equal to or greater** than E_a to reach the transition state. After the transition state has been reached, and as C and D begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules A and B) therefore tends to take place readily once the reaction has started. In Figure **1.6.3**, ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

$$C + D \longrightarrow A + B$$

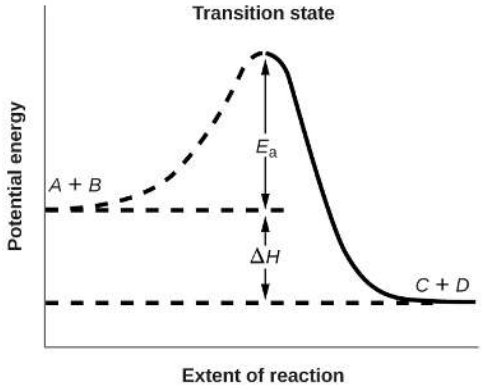


Figure **1.6.3**: This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The curve's peak represents the transition state.

We can use the Arrhenius equation to relate the activation energy and the rate constant, *k*, of a given reaction:

$$k = Ae^{-E_a/RT} \tag{1.6.1}$$

In this equation,

- R is the ideal gas constant, which has a value 8.314 J/mol/K,
- T is temperature on the Kelvin scale,
- E_a is the activation energy in joules per mole,
- e is the constant 2.7183, and
- A is a constant called the frequency factor, which is related to the frequency of collisions and the orientation of the reacting molecules.

Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor *A* is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-E_a/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation (Equation 1.6.1) describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction.

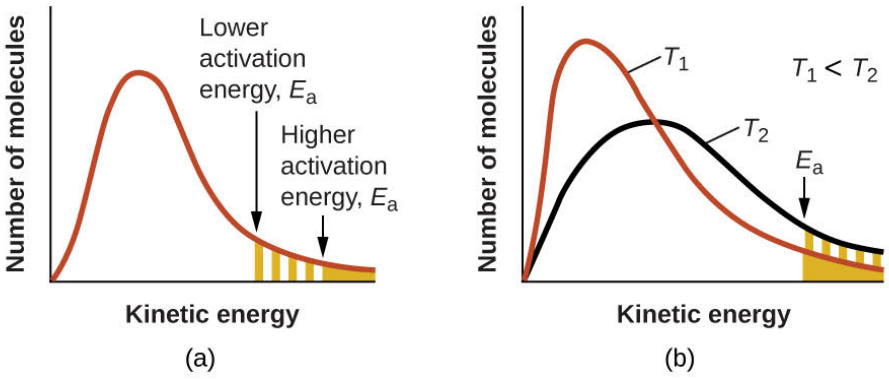


Figure **1.6.4**: (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T2, more molecules have kinetic energies greater than Ea, as shown by the yellow shaded area.

An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure **1.6.4**), as indicated by an increase in the value of $e^{-E_a/RT}$. The rate constant is also directly proportional to the frequency factor, A. Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k.

A convenient approach to determining E_a for a reaction involves the measurement of k at different temperatures and using of an alternate version of the Arrhenius equation that takes the form of linear equation:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$
$$y = mx + b$$

Thus, a plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined. The intercept gives the value of $\ln A$. This is sometimes call an Arrhenius Plot.

Example 1.6.1

Determination of E_a The variation of the rate constant with temperature for the decomposition of HI(g) to $H_2(g)$ and $I_2(g)$ is given here. What is the activation energy for the reaction?

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

variation of the rate constant with temperature for the decomposition of HI(g) to H2(g) and I2(g)

T (K)	k (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of $\frac{1}{T}$ and ln k are:

Solutions to Example 12.5.1

$\frac{1}{T}$ (K^{-1})	ln k
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 1.6.5 is a graph of ln k versus $\frac{1}{T}$. To determine the slope of the line, we need two values of ln k, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of ln k determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is −2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is −14.447.

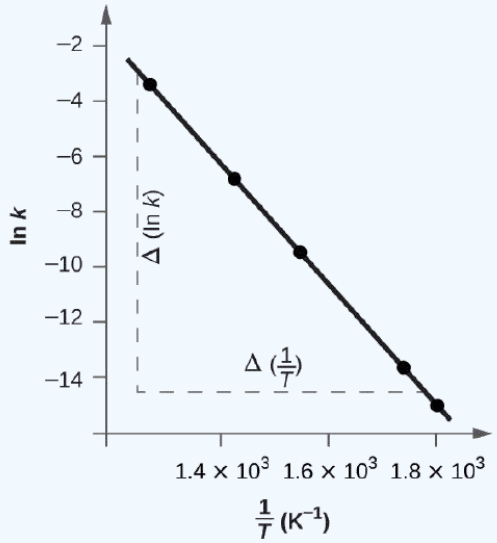


Figure 1.6.5: This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\,HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\begin{aligned} \text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3}\ \text{K}^{-1}) - (1.25 \times 10^{-3}\ \text{K}^{-1})} \\ &= \frac{-11.854}{0.53 \times 10^{-3}\ \text{K}^{-1}} = 2.2 \times 10^{4}\ \text{K} \\ &= -\frac{E_a}{R} \end{aligned}$$

Thus:

$$\begin{aligned} E_a &= -\text{slope} \times R = -(-2.2 \times 10^{4}\ \text{K} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \\ &= 1.8 \times 10^{5}\ \text{J mol}^{-1} \end{aligned}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

can be rearranged as shown to give:

$$\frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$$

or

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

First and Last Entry

T (K)	k (L/mol/s)	$\frac{1}{T}$ (K^{-1})	ln k
555	3.52×10^{-7}	1.80×10^{-3}	−14.860
781	3.95×10^{-2}	1.28×10^{-3}	−3.231

After calculating $\frac{1}{T}$ and ln *k*, we can substitute into the equation:

$$E_a = -8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3}\ \text{K}^{-1} - 1.80 \times 10^{-3}\ \text{K}^{-1}}\right)$$

and the result is E_a = 185,900 J/mol.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

? Exercise 1.6.1

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,N_2O_5(g) \longrightarrow 4\,NO(g) + 3\,O_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer

113,000 J/mol

Summary

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

Key Equations

- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Glossary

activated complex

(also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a)

energy necessary in order for a reaction to take place

Arrhenius equation

mathematical relationship between the rate constant and the activation energy of a reaction

collision theory

model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

frequency factor (A)

proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

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1.7: 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:

$$\begin{aligned} &O_3(g) \longrightarrow O_2(g) + O \\ &O + O_3(g) \longrightarrow 2\,O_2(g) \end{aligned} \tag{1.7.1}$$

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:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{1.7.2}$$

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.

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:

$$A \longrightarrow \text{products} \tag{1.7.3}$$

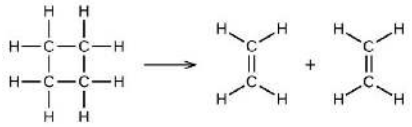
The rate equation for a unimolecular reaction is:

$$\text{rate} = k[A] \tag{1.7.4}$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O \tag{1.7.5}$$

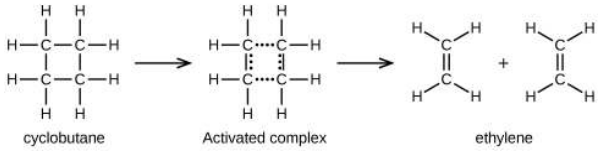
illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, 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:

$$\text{rate} = -\frac{\Delta[C_4H_8]}{\Delta t} = k[C_4H_8] \tag{1.7.6}$$

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.

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:

$$A + B \longrightarrow \text{products} \tag{1.7.7}$$

and

$$2A \longrightarrow \text{products} \tag{1.7.8}$$

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:

$$\text{rate} = k[A][B] \tag{1.7.9}$$

For the second type, in which two identical molecules collide and react, the rate law is second order in A:

$$\text{rate} = k[A][A] = k[A]^2 \tag{1.7.10}$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \tag{1.7.11}$$

(see Figure **1.7.1**)

Figure **1.7.1**: 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:

$$O(g) + O_3(g) \longrightarrow 2\,O_2(g) \tag{1.7.12}$$

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:

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \tag{1.7.13}$$
$$\text{rate} = k[NO]^2[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2\,NO + Cl_2 \longrightarrow 2\,NOCl \tag{1.7.14}$$
$$\text{rate} = k[NO]^2[Cl_2]$$

Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure **1.7.2**.



Figure **1.7.2**: 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 **1.7.1** will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 1.7.1: 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 1.7.1

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.

Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

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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1.8: Catalysis

Learning Objectives

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are thermodynamically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One such reaction is catalytic hydrogenation, the process by which hydrogen is added across an alkene C=C bond to afford the saturated alkane product. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed alkene hydrogenation is shown in Figure 1.8.1.

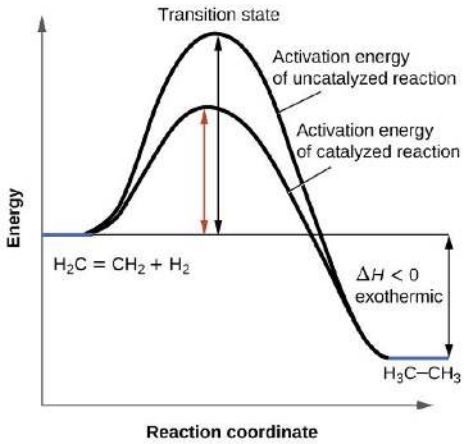


Figure 1.8.1: This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

A graph is shown with the label, “Reaction coordinate,” on the x-axis and the label,“Energy,” on the y-axis. Approximately half-way up the y-axis, a short portion of a black concave down curve which has a horizontal line extended from it across the graph. The left end of this line is labeled “H subscript 2 C equals C H subscript 2 plus H subscript 2.” The black concave down curve extends upward to reach a maximum near the height of the y-axis. The peak of this curve is labeled, “Transition state.” A double sided arrow extends from the horizontal line to the peak of the curve. This arrow is labeled, “Activation energy of Uncatalyzed reation.” From the peak, the curve continues downward to a second horizontally flattened region well below the origin of the curve near the x-axis. This flattened region is shaded in blue and is labeled “H subscript 3 C dash C H subscript 3.” A double sided arrow is drawn from the lowers part of this curve at the far right of the graph to the line extending across the graph above it. This arrow is labeled, “capital delta H less than 0 : exothermic.” A second curve is drawn with the same flattened regions at the start and end of the curve. The height of this curve is about two-thirds the height of the first curve. A double sided arrow is drawn from the horizontal line that originates at the left side of the graph to the peak of this second curve. This arrow is labeled, “Activation energy of catalyzed reaction.”

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in Figure 1.8.2 This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later chapter on chemical equilibrium).

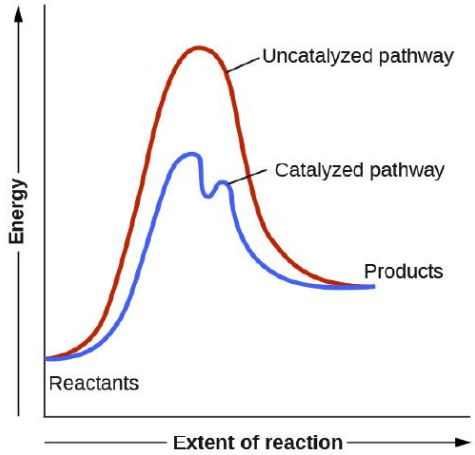
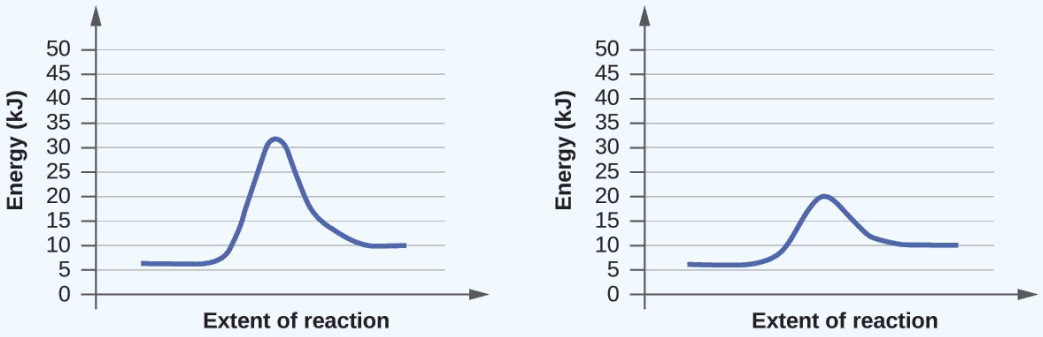


Figure 1.8.2: This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

A graph is shown with the label, “Extent of reaction,” appearing in a right pointing arrow below the x-axis and the label, “Energy,” in an upward pointing arrow just left of the y-axis. Approximately one-fifth of the way up the y-axis, a very short, somewhat flattened portion of both a red and a blue curve are shown. This region is labeled “Reactants.” A red concave down curve extends upward to reach a maximum near the height of the y-axis. This curve is labeled, “Uncatalyzed pathway.” From the peak, the curve continues downward to a second horizontally flattened region at a height of about one-third the height of the y-axis. This flattened region is labeled, “Products.” A second curve is drawn in blue with the same flattened regions at the start and end of the curve. The height of this curve is about two-thirds the height of the first curve and just right of its maximum, the curve dips low, then rises back and continues a downward trend at a lower height, but similar to that of the red curve. This blue curve is labeled, “Catalyzed pathway.”

Example 1.8.1: Using Reaction Diagrams to Compare Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:



In this figure, two graphs are shown. The x-axes are labeled, “Extent of reaction,” and the y-axes are labeled, “Energy (k J).” The y-axes are marked off from 0 to 50 in intervals of five. In a, a blue curve is shown. It begins with a horizontal segment at about 6. The curve then rises sharply near the middle to reach a maximum of about 32 and similarly falls to another horizontal segment at about 10. In b, the curve begins and ends similarly, but the maximum reached near the center of the graph is only 20.

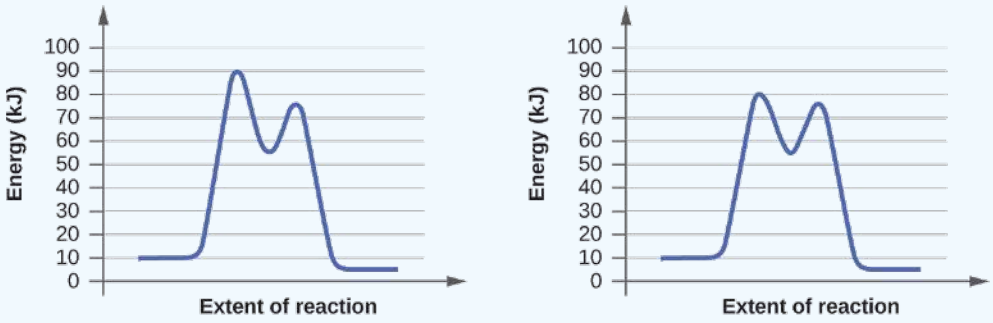
Solution

A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$$E_a = 20\ \text{kJ} - 6\ \text{kJ} = 14\ \text{kJ} \tag{1.8.1}$$

Exercise 1.8.1

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



In this figure, two graphs are shown. The x-axes are labeled, “Extent of reaction,” and the y-axes are labeledc “Energy (k J).” The y-axes are marked off from 0 to 100 at intervals of 10. In a, a blue curve is shown. It begins with a horizontal segment at about 10. The curve then rises sharply near the middle to reach a maximum of about 91, then sharply falls to about 52, again rises sharply to about 73 and falls to another horizontal segment at about 5. In b, the curve begins and ends similarly, but the first peak reaches about 81, drops to about 55, then rises to about 77 before falling to the horizontal region at about 5.

Answer

Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product. As an important illustration of homogeneous catalysis, consider the earth’s ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3\,O_2(g) \xrightarrow{h\nu} 2\,O_3(g) \tag{1.8.2}$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:

$$\begin{aligned} O_3 &\longrightarrow O_2 + O \\ O + O_3 &\longrightarrow 2\,O_2 \end{aligned} \tag{1.8.3}$$

The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:

$$\begin{aligned} NO(g) + O_3(g) &\longrightarrow NO_2(g) + O_2(g) \\ O_3(g) &\longrightarrow O_2(g) + O(g) \\ NO_2(g) + O(g) &\longrightarrow NO(g) + O_2(g) \end{aligned} \tag{1.8.4}$$

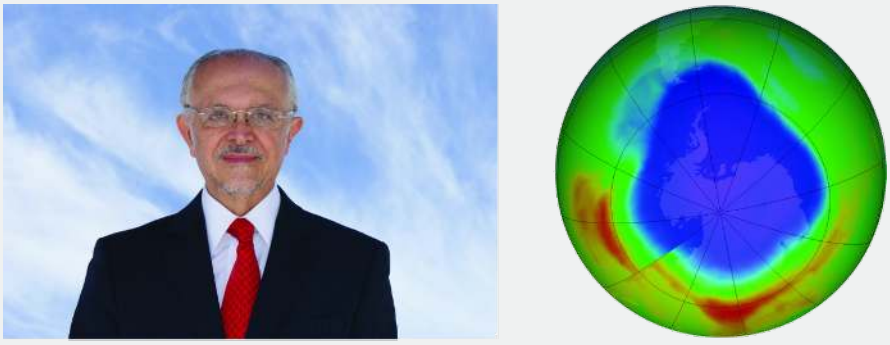
The overall chemical change for the catalyzed mechanism is the same as:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \tag{1.8.5}$$

The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 1.8.3), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone." Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).



(a) (b)

Figure 1.8.3: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

A photograph is shown of Mario Molina. To the right of the photo, an image of Earth's southern hemisphere is shown with a central circular region in purple with a radius of about half that of the entire hemisphere. Just outside this region is a narrow royal blue band, followed by an outer thin turquoise blue band. The majority of the outermost region is green. Two small bands of yellow are present in the lower regions of the image.

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth's upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable "hole" forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth's surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

\[\ce{CH3Cl + OH ⟶ Cl + other\: products} \nonumber \]

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\ce{Cl + O3 ⟶ ClO + O2}$$
$$\ce{ClO + O ⟶ Cl + O2}$$
$$\textbf{overall Reaction: } \ce{O3 + O ⟶ 2\,O2}$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 1.8.4, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (FIgure 1.8.5).

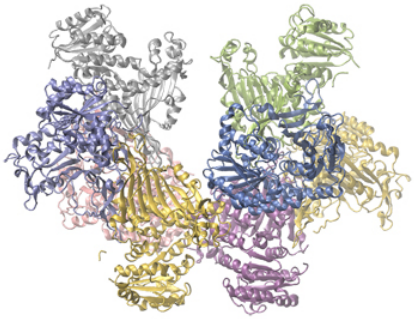


Figure 1.8.4: Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A colorful model of the Glucose-6-phosphate dehydrogenase structure is shown. The molecule has two distinct lobes which are filled with spiraled ribbon-like regions of yellow, lavender, blue, silver, green, and pink.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

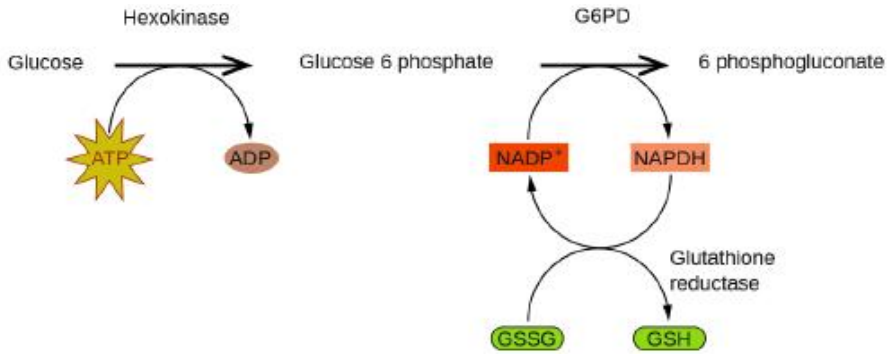


Figure 1.8.5: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NAPDH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

A reaction mechanism is diagrammed in this figure. At the left, the name Glucose is followed by a horizontal, right pointing arrow, labeled, “Hexokinase.” Below this arrow and to the left is a yellow star shape labeled, “A T P.” A curved arrow extends from this shape to the right pointing arrow, and down to the right to a small brown oval labeled, “A D P.” To the right of the horizontal arrow is the name Glucose 6 phosphate, which is followed by another horizontal, right pointing arrow which is labeled, “G 6 P D.” A small orange rectangle below and left of this arrow is labeled “N A D P superscript plus.” A curved arrow extends from this shape to the right pointing arrow, and down to the right to a small salmon-colored rectangle labeled “N A P D H.” A curved arrow extends from this shape below and to the left, back to the orange rectangle labeled, “N A D P superscript plus.” Another curved arrow extends from a green oval labeled “G S S G” below the orange rectangle, up to the arrow curving back to the orange rectangle. This last curved arrow continues on to the lower right to a second green oval labeled, “G S H.” The end of this curved arrow is labeled, “Glutathione reductase.” To the right of the rightmost horizontal arrow appears the name 6 phosphogluconate.

Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

1. Adsorption of the reactant onto the surface of the catalyst
2. Activation of the adsorbed reactant
3. Reaction of the adsorbed reactant
4. Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

Figure 1.8.6 illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

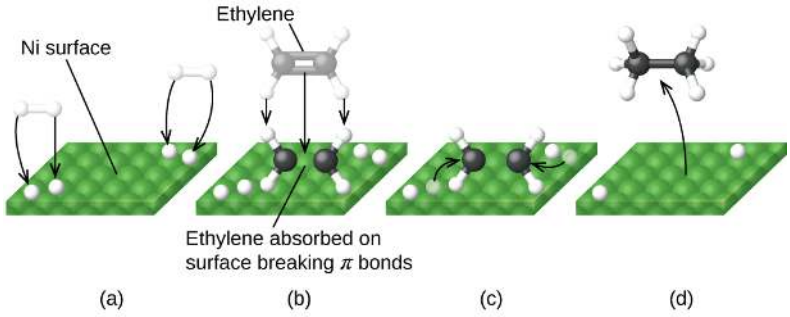


Figure 1.8.6: There are four steps in the catalysis of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ *by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d)* C_2H_6 *molecules escape from the nickel surface, since they are not strongly attracted to nickel.*

In this figure, four diagrams labeled a through d are shown. In each, a green square surface is shown in perspective to provide a three-dimensional appearance. In a, the label “N i surface” is placed above with a line segment extending to the green square. At the lower left and upper right, pairs of white spheres bonded tougher together appear as well as white spheres on the green surface. Black arrows are drawn from each of the white spheres above the surface to the white sphere on the green surface. In b, the white spheres are still present on the green surface. Near the center of this surface is a molecule with two central black spheres with a double bond indicated by two horizontal black rods between them. Above and below to the left and right, a total of four white spheres are connected to the black spheres with white rods. A line segment extends from this structure to the label, “Ethylene absorbed on surface breaking pi bonds.” Just above this is a nearly identical structure greyed out with three downward pointing arrows to the black and white structure to indicate downward motion. The label “Ethylene” at the top of the diagram is connected to the greyed out structure with a line segment. In c, the diagram is very similar to b except that the greyed out structure and labels are gone and one of the white spheres near the black and white structure in each pair on the green surface is greyed out. Arrows point from the greyed out white spheres to the double bond between the two black spheres. In d, only a single white sphere remains from each pair in the green surface. A curved arrow points from the middle of the green surface to a model above with two central black spheres with a single black rod indicating a single bond between them. Each of the black rods has three small white spheres bonded as indicated by white rods between the black spheres and the small white spheres. The four bonds around each black sphere are evenly distributed about the black spheres.

Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, CH_3OH. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 1.8.7).

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 1.8.6).

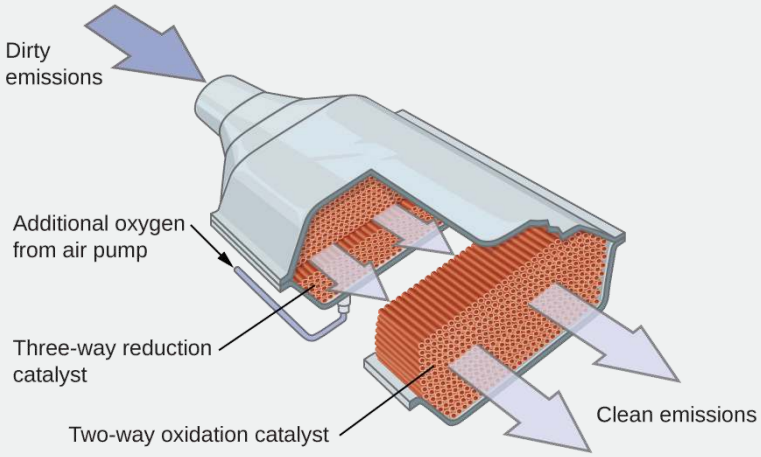


Figure 1.8.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

An image is shown of a catalytic converter. At the upper left, a blue arrow pointing into a pipe that enters a larger, widened chamber is labeled, “Dirty emissions.” A small black arrow that points to the lower right is positioned along the upper left side of the widened region. This arrow is labeled, “Additional oxygen from air pump.” The image shows the converter with the upper surface removed, exposing a red-brown interior. The portion of the converter closest to the dirty emissions inlet shows small, round components in an interior layer. This layer is labeled “Three-way reduction catalyst.” The middle region shows closely packed small brown rods that are aligned parallel to the dirty emissions inlet pipe. The final quarter of the interior of the catalytic converter again shows a layer of closely packed small red brown circles. Two large light grey arrows extend from this layer to the open region at the lower right of the image to the label “Clean emissions.”

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2\,NO_2(g) \longrightarrow N_2(g) + 2\,O_2(g)$$
$$[5pt]2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$
$$[5pt]2\,C_8H_{18}(g) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 1.8.1.

ATP hydrolysis.”" data-quail-id="131" data-mt-width="1016">

Table 1.8.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme's active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 1.8.7).

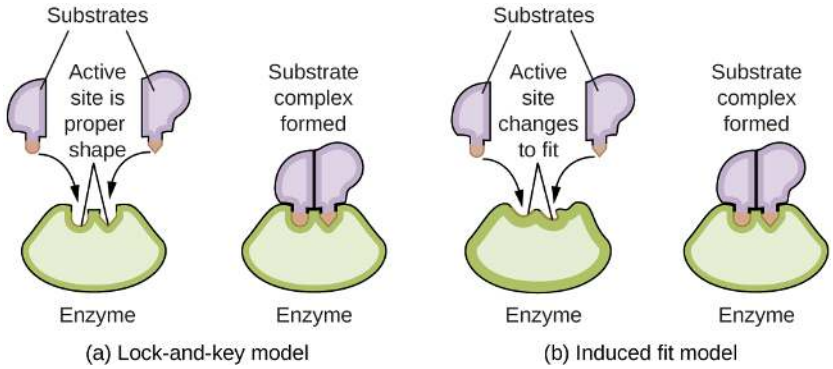


Figure 1.8.7: (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

A diagram is shown of two possible interactions of an enzyme and a substrate. In a, which is labeled "Lock-and-key," two diagrams are shown. The first shows a green wedge-like shape with two small depressions in the upper surface of similar size, but the depression on the left has a curved shape, and the depression on the right has a pointed shape. This green shape is labeled "Enzyme." Just above this shape are two smaller, irregular, lavender shapes each with a projection from its lower surface. The lavender shape on the left has a curved projection which matches the shape of the depression on the left in the green shape below. This projection is shaded orange and has a curved arrow extending from in to the matching depression in the green shape below. Similarly, the lavender shape on the right has a projection with a pointed tip which matches the shape of the depression on the right in the green shape below. This projection is shaded orange and has a curved arrow extending from in to the matching depression in the green shape below. Two line segments extend from the depressions in the green shape to form an inverted V shape above the depressions. Above this and between the lavender shapes is the label, "Active site is proper shape." The label "Substrates" is at the very top of the diagram with line segments extending to the two lavender shapes. To the right of this diagram is a second diagram showing the lavender shapes positioned next to each other, fit snugly into the depressions in the green shape, which is labeled "Enzyme." Above this diagram is the label, "Substrate complex formed." In b, which is labeled "Induced fit," two diagrams are shown. The first shows a green wedge-like shape with two small depressions in the upper surface of similar size, but irregular shape. This green shape is labeled "Enzyme." Just above this shape are two smaller irregular lavender shapes each with a projection from its lower surface. The lavender shape on the left has a curved projection. This projection is shaded orange and has a curved arrow extending from it to the irregular depression just below it in the green shape below. Similarly, the lavender shape on the right has a projection with a pointed tip. This projection is shaded orange and has a curved arrow extending from it to the irregular depression just below it in the green shape below. Two line segments extend from the depressions in the green shape to form an inverted V shape above the depressions. Above this and between the lavender shapes is the label, "Active site changes to fit." The label, "Substrates" is at the very top of the diagram with line segments extending to the two lavender shapes. To the right of this diagram is a second diagram showing the purple shapes positioned next to each other, fit snugly into the depressions in the green shape, which is labeled "Enzyme." Above this diagram is the label "Substrate complex formed." The projections from the lavender shapes match the depression shapes in the green shape, resulting in a proper fit.

Summary

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Footnotes

1. "The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, Nobel Prizes Chemistry [www.nobelprize.org].

Glossary

heterogeneous catalyst

catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst

catalyst present in the same phase as the reactants

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1.E: Kinetics (Exercises)

12.1: Chemical Reaction Rates

Q12.1.1

What is the difference between average rate, initial rate, and instantaneous rate?

Solution

First, a general reaction rate must be defined to know what any variation of a rate is. The reaction rate is defined as the measure of the change in concentration of the reactants or products per unit time. The rate of a chemical reaction is not a constant and rather changes continuously, and can be influenced by temperature. Rate of a reaction can be defined as the disappearance of any reactant or appearance of any product. Thus, an average rate is the average reaction rate over a given period of time in the reaction, the instantaneous rate is the reaction rate at a specific given moment during the reaction, and the initial rate is the instantaneous rate at the very start of the reaction (when the product begins to form).

The instantaneous rate of a reaction can be denoted as

$$\lim_{\Delta t \to 0} \frac{\Delta[concentration]}{\Delta t}$$

Q12.1.2

Ozone decomposes to oxygen according to the equation $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

Solution

For the general reaction, aA ---> bB, the rate of the reaction can be expressed in terms of the disappearance of A or the appearance of B over a certain time period as follows.

$$-\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \tag{1.E.1}$$

We want the rate of a reaction to be positive, but the change in the concentration of a reactant, A, will be negative because it is being used up to be transformed into product, B. Therefore, when expressing the rate of the reaction in terms of the change in the concentration of A, it is important to add a negative sign in front to ensure the overall rate positive.

Lastly, the rate must be normalized according to the stoichiometry of the reaction. In the decomposition of ozone to oxygen, two moles of ozone form three moles of oxygen gas. This means that the increase in oxygen gas will be 1.5 times as great as the decrease in ozone. Because the rate of the reaction should be able to describe both species, we divide the change in concentration by its stoichiometric coefficient in the balanced reaction equation to deal with this issue.

Therefore, the rate of the reaction of the decomposition of ozone into oxygen gas can be described as follows:

$$Rate = -\frac{\Delta[O3]}{2\Delta T} = \frac{\Delta[O2]}{3\Delta T} \tag{1.E.2}$$

Answer

$$Rate=-\frac{\Delta[O3]}{2\Delta T}=\frac{\Delta[O2]}{3\Delta T}\]

Q12.1.3

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3\,F_2(g) \longrightarrow 2\,ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

Solution

In this problem we are asked to write the equation that relates rate expressions in terms of disappearance of the reactants of the equation and in terms of the formation of the product. A reaction rate gives insight to how rate is affected as a function of concentration of the substances in the equation. Rates can often be expressed on graphs of concentration vs time expressed in change (Δ) of concentration and time and in a short enough time interval, the instantaneous rate can be approximated. If we were to analyze the reaction given, the graph would demonstrate that Cl_2 decreases, that F_2 decreases 3 times as quickly, and then ClF_3 increases at a rate doubles. The reactants are being used and converted to product so they decrease while products increase.

For this problem, we can apply the general formula of a rate to the specific aspects of a problem where the general form follows:

$$aA + bB \longrightarrow cC + dD$$

.

And the rate can then be written as $rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$. Here the negative signs are used to keep the convention of expressing rates as positive numbers.

In this specific case we use the stoichiometry to get the specific rates of disappearance and formation (back to what was said in the first paragraph). So, the problem just involves referring the to the equation and its balanced coefficients. Based upon the equation we see that Cl_2 is a reactant and has no coefficient, F_2 has a coefficient of 3 and is also used up, and then ClF_3 is a product that increases two-fold with a coefficient of 2. So, the rate here can be written as:

$$rate = -\frac{\Delta[Cl_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[F_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[ClF_3]}{\Delta t}$$

Answer

$$\text{rate} = +\frac{1}{2}\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$$

Q12.1.4

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$$2\,\text{C}_4\text{H}_6 \longrightarrow \text{C}_8\text{H}_{12}$$

Time (s)	0	1600	3200	4800	6200
$[C_4H_6]$ (M)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?
c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Solution

1.) The average rate of dimerization is the change in concentration of a reactant per unit time. In this case it would be:

$$rate\ of\ dimerization = -\frac{\Delta[C_4H_6]}{\Delta t}$$

Rate of dimerization between 0 s and 1600 s:

$$rate\ of\ dimerization = -\frac{5.04\times10^{-3}M - 1.00\times10^{-2}M}{1600s - 0s}$$

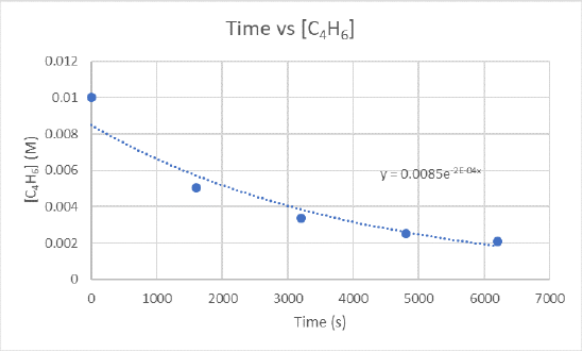
$$rate\ of\ dimerization = 3.10 \times 10^{-6}\frac{M}{s}$$

Rate of dimerization between 1600 s and 3200 s:

$$rate\ of\ dimerization = -\frac{3.37\times10^{-3}M - 5.04\times10^{-3}M}{3200s - 1600s}$$

$$rate\ of\ dimerization = 1.04 \times 10^{-6}\frac{M}{s}$$

2.) The instantaneous rate of dimerization at 3200 s can be found by graphing time versus $[C_4H_6]$.



Because you want to find the rate of dimerization at 3200 s, you need to find the slope between 1600 s and 3200 s and also 3200 s and 4800 s.

For the slope between 1600 s and 3200 s use the points (1600 s, 5.04 x 10^{-3} M) and (3200 s, 3.37 x 10^{-3} M)

$$\frac{3.37\times10^{-3}M-5.04\times10^{-3}M}{3200s-1600s}$$

$$\frac{-0.00167M}{1600s}$$

$$-1.04\times10^{-6}\frac{M}{s}$$

For the slope between 3200 s and 4800 s use the points (3200s, 3.37 x 10^{-3} M) and (4800s, 2.53 x 10^{-3} M)

$$\frac{2.53\times10^{-3}M-3.37\times10^{-3}M}{4800s-3200s}$$

$$\frac{-8.4\times10^{-4}M}{1600s}$$

$$-5.25\times10^{-7}\frac{M}{s}$$

Take the two slopes you just found and find the average of them to get the instantaneous rate of dimerization.

$$\frac{-1.04\times10^{-6}\frac{M}{s}+-5.25\times x10^{-7}\frac{M}{s}}{2}$$

$$\frac{-1.565\times10^{-6}\frac{M}{s}}{2}$$

$$-7.83\times10^{-7}\frac{M}{s}$$

The instantaneous rate of dimerization is $-7.83\times10^{-7}\frac{M}{s}$ and the units of this rate is $\frac{M}{s}$.

3.) The average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s can be found by using our answers from part a and b. If you look back up at the original equation, you could see that C_4H_6 and C_8H_{12} are related in a two to one ratio. For every two moles of C_4H_6 used, there is one mole of C_8H_{12} produced.

For this reaction, the average rate of dimerization and the average rate of formation can be linked through this equation:

$$\frac{-1}{2}\frac{\Delta[C_4H_6]}{\Delta t}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

Notice that reactant side is negative because the reactants are being used up in the reaction.

So, for the average rate of formation of C_8H_{12} at 1600 s, use the rate of dimerization between 0 s and 1600 s we found earlier and plug into the equation:

$$\frac{-1}{2}\times3.10\times10^{-6}\frac{M}{s}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

$$\frac{\Delta[C_8H_{12}]}{\Delta t}=1.55\times10^{-6}\frac{M}{s}$$

The average rate of formation for C_8H_{12} at 1600 s is $1.55\times10^{-6}\frac{M}{s}$. The rate of formation will be positive because products are being formed.

The instantaneous rate of formation for C_8H_{12} can be linked to the instantaneous rate of dimerization by this equation:

$$\frac{-1}{2}\frac{d[C_4H_6]}{dt}=\frac{d[C_8H_{12}]}{dt}$$

So, for the instantaneous rate of formation for C_8H_{12} at 3200 s, use the value of instantaneous rate of dimerization at 3200 s found earlier and plug into the equation:

$$\frac{-1}{2} \times -7.83 \times 10^{-7} \frac{M}{s} = \frac{d[C_8H_{12}]}{dt}$$

$$\frac{d[C_8H_{12}]}{dt} = -3.92 \times 10^{-7} \frac{M}{s}$$

The instantaneous rate of formation for C_8H_{12} at 3200 s is $-3.92 \times 10^{-7} \frac{M}{s}$

Answer

a. $3.10 \times 10^{-6} \frac{M}{s}$ and $1.04 \times 10^{-6} \frac{M}{s}$
b. $-7.83 \times 10^{-7} \frac{M}{s}$ and $\frac{M}{s}$
c. $-3.92 \times 10^{-7} \frac{M}{s}$

Q12.1.5

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.952	0.625	0.465	0.370	0.308	0.230

a. Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*]. What are the units of this rate?
c. Use the rates found in parts (a) and (b) to determine the average rate of formation of *B* between 0.00 s and 10.0 s, and the instantaneous rate of formation of *B* at 15.0 s.

Solution

Equations: $\frac{-\triangle A}{\triangle time}$ and Rate=$\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$

Solve: 1.)The change in A from 0s to 10s is .625-1=-.375 so $\frac{-\triangle A}{\triangle time}$=.375/10= **0.0374 M/s**

Similarly, the change in A from 10 to 20 seconds is .370-.625=-.255 so $\frac{-\triangle A}{\triangle time}$=.255/20-10= **0.0255M/s**

2.) We can estimate the rate law graphing the points against different order equations to determine the right order.

Zero Order:

$$\frac{d[A]}{dt} = -k$$

$$\int_{A_\circ}^{A} d[A] = -k \int_0^t dt$$

$$[A] = -kt + [A_\circ]$$

First Order:

$$\frac{d[A]}{dt} = -k[A]$$

$$\int_{A_\circ}^{A} \frac{d[A]}{[A]} = -kdt$$

$$Ln(A) = -kt + Ln(A_\circ)$$

Second Order:

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\int_{A_\circ}^{A} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A_\circ]}$$

Now that we have found the linear from of each order we will plot the points vs an [A] y-axis, a Ln(A) y-axis, and a 1/[A] y-axis. whichever of the plots has the most linear points will give us a good idea of the order and the slope will be the k value.



Here we notice that the second order is most linear so we conclude the Rate to be..

$$\frac{-d[A]}{2dt} = k[A]^2$$

At 15 seconds [A]=.465 and from the slope of the graph we find k=.116.so if we plug this data in and multiply both sides by 2 to get rid of the 2 in the denominator on the left side of the equation we find that the rate of disappearance of A is .05 M/s where the units are equivalent to [mol*L^{-1}*s^{-1}]

3.) Using the equation $\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$ we divide the rates in part a and b in half to get .0188 M/s from 0 to 10 seconds and .025 M/s for the estimated instantaneous rate at 15s.

Answer

(a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 12 − 18 s = 0.0225 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.0500 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.0250 mol L^{-1} s^{-1}

Q12.1.6

Consider the following reaction in aqueous solution:

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4}\ M\ s^{-1}$, what is the rate of appearance of $Br_2(aq)$ at that moment?

Solution

Step 1. Define the rate of the reaction.

Recall:

For the general reaction: aA + bB → cC+ dD

$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$

So, for the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$

The rate would be: $rate = -\frac{\Delta[Br^-]}{5\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{\Delta[H^+]}{6\Delta t} = \frac{\Delta[Br_2]}{3\Delta t} = \frac{H_2O}{3\Delta t}$

Step 2. Since we are given the rate for the disappearance of Br^-(aq) is $3.5x10^-4Ms^{-1}$, and we want to find the rate of appearance of Br_2(aq). Therefore we set the two rates equal to each other.

$$rate = -\frac{\Delta[Br^-]}{5\Delta t} = \frac{\Delta[Br_2]}{3\Delta t}$$

And, $-\frac{\Delta[Br^-]}{\Delta t} = -3.5x10^{-4}Ms^{-1}$

So, $3.5x10^{-4}Ms^{-1} = \frac{5}{3}\frac{\Delta[Br_2]}{\Delta t}$

Step 3. Now solve the equation.

$$\frac{(3.5x10^{-4})(3)}{5} = \frac{\Delta[Br_2]}{\Delta t}$$

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

Answer

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

12.2: Factors Affecting Reaction Rates

Q12.2.1

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Solution

Molarity of Hydrochloric Acid

- Reaction rates are affected by the frequency at which molecules collide. High Molarity=High Concentration which means more molecules are available to collide thus a faster reaction that one with a low molarity of HCl at a fixed volume.

Temperature of Solution

- Higher temperatures increase the rate of reaction because molecules move faster thus colliding more frequently
- increasing temperatures allows for more particles to move past activation energy barrier to start the reaction

Size of pieces of Magnesium

- reaction rate is dependent on solid reactant size; smaller pieces increases the chance of collision because they enable a greater surface area thus faster reaction rate

Q12.2.2

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

a. What happens when the angle of the collision is changed?
b. Explain how this is relevant to rate of reaction.

Solution

According to the collision theory, there are many factors that cause a reaction to happen, with three of the factors being how often the molecules or atoms collide, the molecules' or atoms' orientations, and if there is sufficient energy for the reaction to happen. So, if the angle of the plunger is changed, the atom that is shot (a lone Oxygen atom in this case) will hit the other molecule (CO in this case) at a different spot and at a different angle, therefore changing the orientation and the number of proper collisions will most likely not cause for a reaction to happen. Thanks to the simulation, we can see that this is true: depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other (no reaction happens).

In this particular case, the rate of the reaction will decrease because, by changing the angle, the molecules or atoms won't collide with the correct orientation or as often with the correct orientation.

Q12.2.3

In the PhET Reactions & Rates interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

S12.2.3

Based on the Collision Theory, a reaction will only occur if the molecules collide with proper orientation and with sufficient energy required for the reaction to occur. The minimum energy the molecules must collide with is called the activation energy (energy of transition state).

Increasing the concentration of reactants increases the probability that reactants will collide in the correct orientation since there are more reactants in the same volume of space. Therefore, increasing the concentration of reactants would increase the rate of the reaction. Decreasing the concentration of reactants would decrease the rate of reaction because the overall number of possible collisions would decrease.

Temperature is directly related the the kinetic energy of molecules and activation energy E_a is the minimum energy required for a reaction to occur and doesn't change for a reaction. Increasing the temperature increases the kinetic energy of the reactants meaning the reactants will move faster and collide with each other more frequently. Therefore, increasing the temperature increase the rate of the reaction. Decreasing the temperature decreases the rate of reaction since the molecules will have less kinetic energy, move slower, and therefore collide with each other less frequently.

Q12.2.4

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

a. Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?
b. Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

Solution

a. On the simulation, we select the default setting and the reaction A+BC. In the default setting, we see frequent collisions, a low initial temperature, and a total average energy lower than the energy of activation. The collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Although we see moving and frequently colliding reactants, the rate of the forward reaction is actually slow because it takes a long time for the products, AB and C, to start appearing. This is mainly because the fractions of collisions with required energy is low, coming from the average energy of the molecules being lower than the energy of activation.

b. The reaction proceeds at an even faster rate. Again, the collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Because molecules have a higher amount of energy, they have more kinetic energy. With an increased kinetic energy, the molecules not only collide more but also increase in the fraction of collision. However, the forward reaction and the backward reaction both proceed at a fast rate, so both happen almost simultaneously. It takes a shorter time for both reactions to happen. With both of the reactions adding up together overall, there is eventually a state of equilibrium. The process at which equilibrium is reached, however, is faster. Therefore, the amount of products of A+BC stays the same after a while.

12.3: Rate Laws

Q12.3.1

How do the rate of a reaction and its rate constant differ?

S12.3.1

The rate of a reaction or reaction rate is the change in the concentration of either the reactant or the product over a period of time. If the concentrations change, the rate also changes.

Rate for A → B:

$$rate = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

The rate constant (k) is a proportionality constant that relates the reaction rates to reactants. If the concentrations change, the rate constant does not change.

For a reaction with the general equation: $aA + bB \rightarrow cC + dD$

the experimentally determined rate law usually has the following form:

$$rate = k[A]^m[B]^n$$

Q12.3.2

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution

(a) 2; (b) 1

Q12.3.3

Tripling the concentration of a reactant increases the rate of a reaction nine times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four times. What is the order of the reaction with respect to that reactant?

Q12.3.4

How much and in what direction will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}]^2$?

a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

Q12.3.5

How will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$?

a. Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
b. Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

Q12.3.6

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to

depletion of the ozone layer. The reaction $\mathbf{NO + O_3 \longrightarrow NO_2 + O_2}$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3×10^{-6} *M* and [O_3] = 5.9×10^{-7} *M*?

Solution

4.3×10^{-5} mol/L/s

Q12.3.7

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$$\mathbf{^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-}$$

Rate = 4.85×10^{-2} $\mathbf{day^{-1}}$ $\mathbf{[^{32}P]}$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

Q12.3.8

The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} $year^{-1}$. The products of the decay are nitrogen atoms and electrons (beta particles):

$$\mathbf{^{6}_{14}C \longrightarrow {}^{6}_{14}N + e^-}$$

$$\mathbf{rate = \mathit{k}[^{6}_{14}C]}$$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5×10^{-9} *M*?

Solution

7.9×10^{-13} mol/L/year

Q12.3.9

What is the instantaneous rate of production of N atoms Q12.3.8 in a sample with a carbon-14 content of 1.5×10^{-9} *M*?

Q12.3.10

The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L/mol/s. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55×10^{-4} *M*?

Q12.3.11

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate (mol/L/h)	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Solution

rate = *k*; $k = 2.0 \times 10^{-2}$ mol/L/h (about 0.9 g/L/h for the average male); The reaction is zero order.

Q12.3.12

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[NH_3]$ (M)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol/L/h^1)	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Q12.3.13

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2\,NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$

Determine the rate equation, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (M)	0.10	0.20	0.30
Rate (mol/L/h)	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution

Before we can figure out the rate constant first we must first determine the basic rate equation and rate order. The basic rate equation for this reaction, where n is the rate order of NOCl and k is the rate constant, is

$$rate = k[NOCl]^n$$

since NOCl is the reactant in the reaction.

In order to figure out the order of the reaction we must find the order of [NOCl] as it is the only reactant in the reaction. To do this we must examine how the rate of the reaction changes as the concentration of NOCl changes.

As [NOCl] doubles in concentration from 0.10 M to 0.20 M the rate goes from 8.0 x 10^{-10} to 3.2 x 10^{-9}

(3.2 x 10^{-9}(mol/L/h))/(8.0 x 10^{-10}(mol/L/h)) = 4

so we conclude that as [NOCl] doubles, the rate goes up by 4. Since 2^2= 4 we can say that the order of [NOCl] is 2 so our updated rate law is

$$rate = k[NOCl]^2$$

Now that we have the order, we can substitute the first experimental values from the given table to find the rate constant, k

(8.0 x 10^{-10}(mol/L/h)) = k(0.10 M)^2 so

$$k = \frac{8.0 \times 10^{-10}}{(0.10\,M)^2} = 8 \times 10^{-8} M^{-1} sec^{-1}$$

We were able to find the units of k using rate order, when the rate order is 2 units of k are M^{-1} x sec^{-1}

So the rate equation is: rate = k[NOCl]^2, it is second order, and k = 8 x 10^{-8} M^{-1} x sec^{-1}

Overall rate law :

$$rate = \underbrace{(8 \times 10^{-8})}_{1/(M \text{ x sec})}[NOCl]^2$$

Answer

rate = k[NOCl]^2; k = 8.0 × 10^{-8} L/mol/s; second order

https://chem.libretexts.org/@go/page/210143

Q12.3.14

From the following data, determine the rate equation, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

[*A*] (*M*)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol/L/h)	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Solution

A. Using the experimental data, we can compare the effects of changing [A] on the rate of reaction by relating ratios of [A] to ratios of rates

$$\frac{2.66 \times 10^{-2}}{1.33 \times 10^{-2}} = 2$$

and

$$\frac{1.52 \times 10^{-6}}{3.8 \times 10^{-7}} = 4$$

B. From this we know that doubling the concentration of A will result in quadrupling the rate of reaction. The order of this reaction is 2.

C. We can now write the rate equation since we know the order:

$$rate = k[A]^2$$

D. By plugging in one set of experimental data into our rate equation we can solve for the rate constant, k:

$$3.8 \times 10^{-7} = k \times (1.33 \times 10^{-2})^2$$

$$k = \frac{3.8 \times 10^{-7}}{1.769 \times 10^{-4}}$$

$$k = .00215 M^{-1} s^{-1}$$

Answer

$k = .00215 M^{-1} s^{-1}$

2nd Order

Q12.3.15

Nitrogen(II) oxide reacts with chlorine according to the equation:

$$2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L^1)	[Cl_2] (mol/L)	Rate (mol/L/h)
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate equation that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

Solution

For the general equation,

$aA + bB \rightarrow cC + dD$

The rate can be written as

$rate = k[A]^m[B]^n$ where k is the rate constant, and m and n are the reaction orders.

For our equation

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

the $rate = k[NO]^m[Cl_2]^n$

Now, we need to find the reaction orders. Reaction orders can only be found through experimental values. We can compare two reactions where one of the reactants has the same concentration for both trials, and solve for the reaction order.

$\frac{rate_1}{rate_2} = \frac{[NO]_1^m[Cl_2]_1^n}{[NO]_2^m[Cl_2]_2^n}$

We can use the data in the table provided. If we plug in the values for rows 1 and 2, we see that the values for the concentration of Cl will cancel, leaving just the rates and the concentrations of NO.

$\frac{1.14}{4.56} = \frac{[0.5]^m}{[1.0]^m}$

We can now solve for m, and we find that m =2. This means that the reaction order for [NO] is 2.

Now we must find the value of n. To do so, we can use the same equation but with the values from rows 2 and 3. This time, the concentration of NO will cancel out.

$\frac{4.56}{9.12} = \frac{[0.5]^n}{[1.0]^n}$

When we solve for n, we find that n = 1. This means that the reaction order for $[Cl_2]$ is 1.

We are one step closer to finishing our rate equation.

$rate = k[NO]^2[Cl_2]$

Finally, we can solve for the rate constant. To do this, we can use one of the trials of the experiment, and plug in the values for the rate, and concentrations of reactants, then solve for k.

$1.14 mol/L/h = k[0.5 mol/L]^2[0.5 mol/L]$

$k = 9.12 L^2 mol^{-2} h^{-1}$

So, our final rate equation is:

$rate = (9.12 L^2 mol^{-2} h^{-1})[NO]^2[Cl_2]$

*A common mistake is forgetting units. Make sure to track your units throughout the process of determining your rate constant. Be careful because the units will change relative to the reaction order.

Answer

rate = $k[NO]^2[Cl]_2$; k = 9.12 L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

Q12.3.17

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

$$H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol/L/s)	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Solution

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Determine the rate equation, the rate constant, and the orders with respect to each reactant.

The rate constant and the orders can be determined through the differential rate law. The general form of the differential rate law is given below:

aA + bB + cC ==> products

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^n[B]^m[C]^p$$

where A, B, and C are the concentrations of the reactants, k is the rate constant, and n,m, and p refer to the order of each reactant.

To find the orders of each reactant, we see that when [NO] doubles but $[H_2]$ doesn't change, the rate quadruples, meaning that [NO] is a second order reaction ($[NO]^2$). When $[H_2]$ doubles but [NO] doesn't change, the rate doubles, meaning that $[H_2]$ is a first order reaction. So the rate law would look something like this:

$$\text{Rate} = k[NO]^2[H_2]$$

We can use this rate law to determine the value of the rate constant. Plug in the data for reactant concentration and rate from one of the trials to solve for k the rate constant. In this case, we chose to use the data from trial 1 from the second column of the data table.

$$2.835\text{x}10^{-3} = k[0.3]^2[0.35]$$

$$k = .09\ M^{-2}/s^{-1}$$

Q12.3.18

For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[A] (M)	0.230	0.356	0.557
Rate (mol/L/s)	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

a. What is the order of the reaction with respect to [*A*], and what is the rate equation?
b. What is the rate constant?

Solution

1. The rate equation for an n order reaction is given as $\frac{dr}{dt} = k[A]^n$. Where $[A]$ is the concentration in M, and $\frac{dr}{dt}$ is the rate in M/s.

We can then use each set of data points, plug its values into the rate equation and solve for n. Note you can use any of the data points as long as the concentration corresponds to its rate.

Rate equation 1: $4.17 \times 10^{-4} = k[0.230]^n$

Rate equation 2: $9.99 \times 10^{-4} = k[0.356]^n$

We divide Rate equation 1 by Rate equation 2 in order to cancel out k, the rate constant.

$$\frac{4.17\times10^{-4}}{9.99\times10^{-4}} = \frac{k[0.230]^n}{k[0.356]^n}$$

$$0.417 = 0.646^n$$

Now the only unknown we have is n. Using logarithm rules one can solve for it.

$$ln\ 0.417 = n \cdot ln\ 0.646$$

$$\frac{ln\ 0.417}{ln\ 0.646} = n = 2$$

The rate equation is second order with respect to A and is written as $\frac{dr}{dt} = k[A]^2$.

2. We can solve for k by plugging in any data point into our rate equation $\frac{dr}{dt} = k[A]^2$.

Using the first data points for instance $[A] = 0.230 \ \frac{mol}{L}$ and $\frac{dr}{dt} = 4.17 \times 10^{-4} \ \frac{mol}{L \cdot s}$] we get the equation $4.17 \times 10^{-4} \ \frac{mol}{L \cdot s} = k[0.230 \ \frac{mol}{L}]^2$

Which solves for $k = 7.88 \times 10^{-3} \frac{L}{mol \cdot s}$

Since we know this is a second order reaction the appropriate units for k can also be written as $\frac{1}{M \cdot s}$

Answer

(a) The rate equation is second order in A and is written as rate = $k[A]^2$. (b) k = 7.88 × 10^{-13} L mol^{-1} s^{-1}

Q12.3.19

For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{initial}$ (M)	0.170	0.212	0.357
Rate (mol/L/s)	6.68 × 10^{-3}	1.04 × 10^{-2}	2.94 × 10^{-2}

a. What is the order of the reaction with respect to [Q], and what is the rate equation?
b. What is the rate constant?

Solution

What is the order of the reaction with respect to [Q], and what is the rate equation?

- Order reaction: 2 because when you use the ratio trial 3:2, it will look like this:
- $(\frac{2.94 * 10^{-2}}{1.04 * 10^{-2}}) = (\frac{0.357^x}{0.212^x})$
- 2.82 = 1.7^x
- x = 2 so the order of reaction is 2
- Rate reaction equation: Rate=k[Q]^2

What is the rate constant?

- To find the rate constant (k) simply plug and calculate one of the trials into the rate equation
- 1.04 x 10^{-2}=k[0.212]^2
- k=0.231 $M^{-1}s^{-1}$

Answer

Order: 2

k=0.231 $M^{-1}s^{-1}$

Q12.3.20

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2 × 10^{-4} min^{-1}.

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

What is the rate of the reaction when [N_2O_5] = 0.40 M?

Solution

Step 1: The first step is to write the rate law. We know the general formula for for a first-order rate law. It is as follows: Rate=k[A]

Step 2: We now plug in [N_2O_5] in for [A] in our general rate law. We also plug in our rate constant (k), which was given to us. Now our equation looks as follows:

Rate=(6.2x10^{-4} min^{-1})[N_2O_5]

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Step 3: We now plug in our given molarity. $[N_2O_5]$=0.4 M. Now our equation looks as follows:

Rate=$(6.2x10^{-4}\ min^{-1})(0.4\ M)$

Step 4: We now solve our equation. Rate=$(6.2x10^{-4}\ min^{-1})(0.4\ M)= 2.48x10^{-4}$ M/min.
Step 5: Use significant figures and unit conversion to round $2.48x10^{-4}$ M/min to 2.5×10^{-4} (moles)$L^{-1}min^{-1}$

Answer

(a) 2.5×10^{-4} mol/L/min

Q12.3.21

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

a. $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$
b. $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$
c. $3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} $L^2/mol^2/s$.

Solution

To determine the rate law for an equation we need to look at its slow step. Since both equation a and c are fast, equation b can be considered the slow step of the reaction. The slow step is also considered the rate determining step of the system.

Hence, The rate determining step is the second step because it's the slow step.

rate of production of $NO_2 = k[A]^m[B]^n$

$rate = k[NO]^2[O_2]^1\ M/s$

$rate = (5.8 * 10^{-6})[0.75]^2[0.5]^1\ M/s$

$rate = 1.6 * 10^{-6}\ M/s$

Answer

$rate = 1.6 * 10^{-6}\ M/s$

Q12.3.22

The following data have been determined for the reaction:

$$I^- + OCl^- \longrightarrow IO^- + Cl^-$$

	1	2	3
$[I^-]_{initial}$ (*M*)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (*M*)	0.050	0.050	0.010
Rate (mol/L/s)	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate equation and the rate constant for this reaction.

Solution

Using the reactants, we can form the rate law of the reaction: $$ r=k[OCl^-]^n[I^-]^m \]

From there, we need to use the data to determine the order of both $[OCl^-]$ and $[I^-]$. In doing so, we need to compare r_1 to r_2 such that:

$$\frac{r_1}{r_2} = \frac{(0.10^m)(0.050^n)}{(0.20^m)(0.050^n)} = \frac{3.05 \times 10^{-4}}{6.20 \times 10^{-4}} \tag{1.E.3}$$

$$0.5^m = 0.5 \tag{1.E.4}$$

$$m = 1 \tag{1.E.5}$$

We can "cross out" the concentration of $[OCl^-]$ because it has the same concentration in both of the trials used.

Now that we know m ($[I^-]$) has a first order of 1.

We cannot "cross out" $[I^-]$ to find $[OCl^-]$ because no two trials have the same concentration. In order to solve for n we will plug in 1 for m.

$$\frac{r_1}{r_3} = \frac{(0.10^1)(0.050^n)}{(0.30^1)(0.010^n)} = \frac{3.05 \times 10^{-4}}{1.83 \times 10^{-4}} \tag{1.E.6}$$

$$\frac{1}{3}(5^n) = 1.6666667 \tag{1.E.7}$$

$$5^n = 5 \tag{1.E.8}$$

$$n = 1 \tag{1.E.9}$$

Since we know that orders of both n and m are equal to one, we can not substitute them into the rate law equation along with the respective concentrations (from either the first, second, or third reaction) and solve for the rate constant, k.

$$r = k[OCl^-]^n[I^-]^m \tag{1.E.10}$$

$$3.05 * 10^{-4} = k[0.05]^1[0.10]^1 \tag{1.E.11}$$

$$k = 6.1 * 10^{-2} \frac{L}{mol \times s} \tag{1.E.12}$$

Thus the overall rate law is: $$ r = (6.1 * 10^{-2} \frac {L}{mol \times s})[OCl^-][I^-] \]

The units for K depend on the overall order of the reaction. To find the overall order we add m and n together. By doing this we find an overall order of 2. This is why the units for K are $$ \frac {L}{mol \times s} \]

Answer

rate = $k[I^-][OCl^{-1}]$; k = 6.1 × 10^{-2} L mol $^{-1}$ s^{-1}

Q12.3.23

In the reaction

$$2NO + Cl_2 \rightarrow 2NOCl$$

the reactants and products are gases at the temperature of the reaction. The following rate data were measured for three experiments:

Initial p{NO}$	Initial $p\{Cl_2\}$	Initial rate
(atm)	(atm)	(moles of A consumed atm sec^{-1})
0.50	0.50	5.1 x 10^{-3}
1.0	1.0	4.0 x 10^{-2}
0.50	1.0	1.0 x 10^{-2}

a. From these data, write the rate equation for this gas reaction. What order is the reaction in NO, Cl_2, and overall?
b. Calculate the specific rate constant for this reaction.

Solution

a. The rate equation can be determined by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine *k* and the exponents *m* and *n* in the following equation:

$$rate = k[A]^m[B]^n$$

To do this, the initial concentration of B can be kept constant while varying the initial concentration of A and calculating the initial reaction rate. This information would deduce the reaction order with respect to A. The same process can be done to find the reaction order with respect to B.
In this particular example,

$$\frac{rate_2}{rate_3} = \frac{k[A_2]^m[B_2]^n}{k[A_3]^m[B_3]^n}$$

So taking the values from the table,

$$\frac{4.0 * 10^{-2}}{1.0 * 10^{-2}} = \frac{k[1.0]^m[1.0]^n}{k[0.5]^m[1.0]^n}$$

and by canceling like terms, you are left with

$$\frac{4.0 * 10^{-2}}{1.0 * 10^{-2}} = \frac{[1.0]^m}{[0.5]^m}$$

Now, solve for m

$4 = 2^m \Longrightarrow m = 2$ Because m=2, the reaction with respect to *NO* is 2. ***NO* is second order.**

You can repeat the same process to find n.

$$\frac{rate_3}{rate_1} = \frac{k[A_3]^m[B_3]^n}{k[A_1]^m[B_1]^n}$$

Taking the values from the table,

$$\frac{1.0 * 10^{-2}}{5.1 * 10^{-3}} = \frac{k[0.5]^m[1.0]^n}{k[0.5]^m[0.5]^n}$$

and by canceling like terms, you are left with

$$\frac{1.0 * 10^{-2}}{5.1 * 10^{-3}} = \frac{[1.0]^n}{[0.5]^n}$$

Now this time, solve for n

$2 = 2^n \implies n = 1$

Because n=1, the reaction with respect to Cl_2 is 1. **Cl_2 is first order.**

So the rate equation is

$$rate = k[NO]^2[Cl_2]^1$$

To find the overall rate order, you simply add the orders together. Second order + first order makes the **overall reaction third order.**

b. The rate constant is calculated by inserting the data from any row of the table into the experimentally determined rate law and solving for k. For a third order reaction, the units of k are $frac1atm^2 * sec$. Using Experiment 1,

$$rate = k[NO]^2[Cl_2]^1 \implies 5.1 * 10^{-3} \frac{atm}{sec} = k[0.5matm]^2[0.5atm]^1$$

$$k = 0.0408 \frac{1}{atm^2 * sec}$$

Answer

NO is second order.

Cl_2 is first order.

Overall reaction order is three.

b)

$k = 0.0408\ atm^{-2} * sec^{-1}$

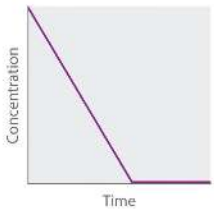
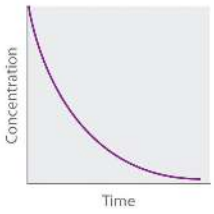
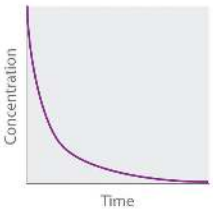
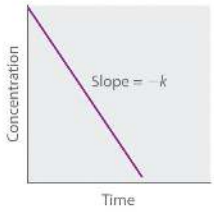
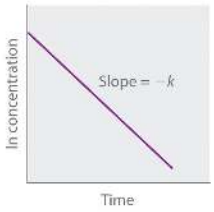
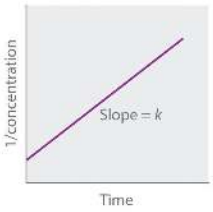
12.4: Integrated Rate Laws

Q12.4.1

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

Solution

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	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], *M* / Rate, M/s 1 / 1 2 / 1 3 / 1	[A], *M* / Rate, M/s 1 / 1 2 / 2 3 / 3	[A], *M* / Rate, M/s 1 / 1 2 / 4 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of *k*, rate constant	M/s	1/s	$M^{-1}\cdot s^{-1}$

To determine the order of a reaction when given the data series, one must graph the data how it is, graph it as natural log of [A], and graph it as 1/[A]. Whichever method yields a straight line will determine the order. Respective of the methods of graphing above, if a straight line is yielded by the first graphing method its a 0 order, if by the second method it's a 1st order, and the third graphing method its a 2nd order. When the order of the graph is known, a series of equations, given in the above image, can be used with the various points on the graph to determine the value of k. We can see that we need an initial value of A and a final value of A, and both of these would be given by the data.

Zeroth order when plotting initial concentrating versus final concentration you have a negative linear slope.

$$[A] = [A]_0 - kt$$

First order when plotting ln[initial concentration] versus ln[final concentration] you have a negative linear slope.

$$\ln[A] = \ln[A]_0 - kt$$

Second order when plotting the 1/[initial concentration] versus 1/[final concentration] you have a positive linear slope.

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Q12.4.2

Use the data provided to graphically determine the order and rate constant of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4	2.50×10^4	3.00×10^4	4.00×10^4
$[SO_2Cl_2]$ (M)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415

Solution

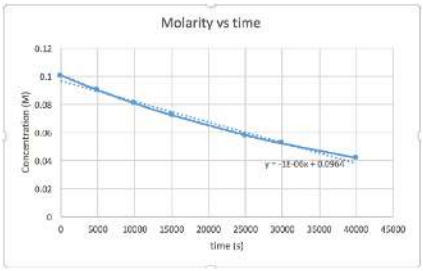
Use the data to graphically determine the order and rate constant of the following reaction.

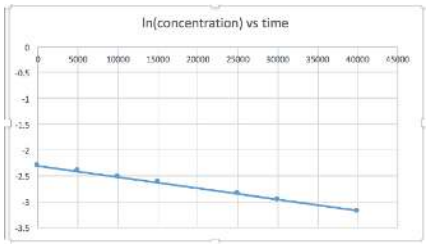
In order to determine the rate law for a reaction from a set of data consisting of concentration (or the values of some function of concentration) versus time, make three graphs of the data based on the integrated rate laws of each order reaction.

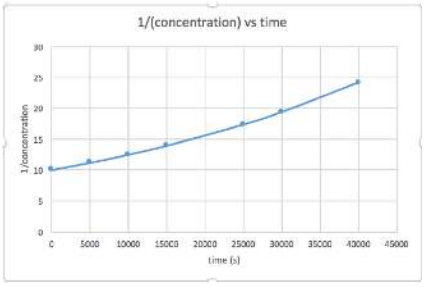
[concentration] versus time (linear for a zero order reaction) ln [concentration] versus time (linear for a 1st order reaction) 1 / [concentration] versus time (linear for a 2nd order reaction)

slope= -2.0 x 10^{-5}

k = 2.0 x 10^{-5}





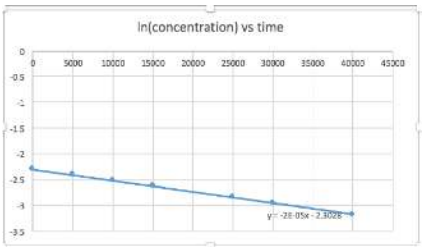


The graph that is linear indicates the order of the reaction. Then, you can find the correct rate equation:

zero order reaction	rate = k	(k = - slope of line)
1st order reaction	rate = k[A]	(k = - slope of line)
2nd order reaction	rate = $k[A]^2$	(k = slope of line)

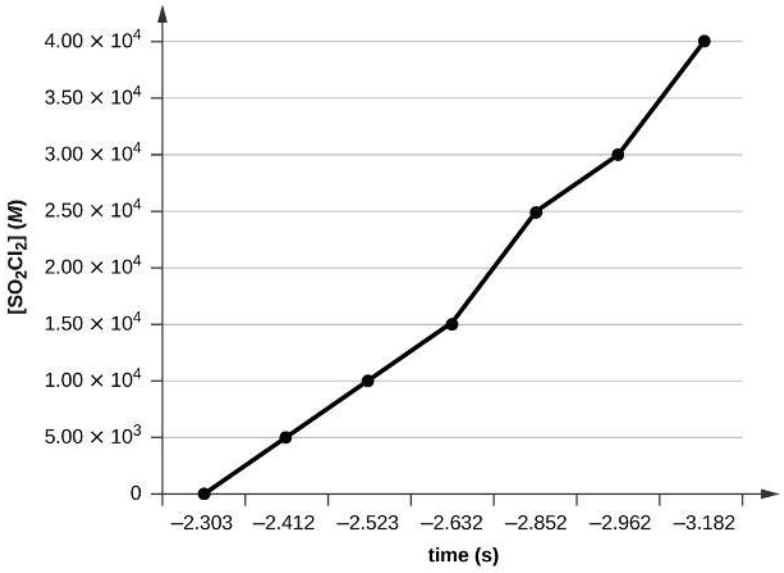
In this graph, ln(concentration) vs time is linear, indicating that the **reaction is first order**.

k=-slope of line



Answer

Plotting a graph of $\ln[SO_2Cl_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:



$k = -2.20 \times 10^5\ s^{-1}$

Q12.4.3

Use the data provided in a graphical method to determine the order and rate constant of the following reaction:

$$2P \longrightarrow Q + W$$

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077×10^{-3}	1.068×10^{-3}	1.055×10^{-3}	1.046×10^{-3}	1.039×10^{-3}

Solution

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Q12.4.4

Pure ozone decomposes slowly to oxygen, $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

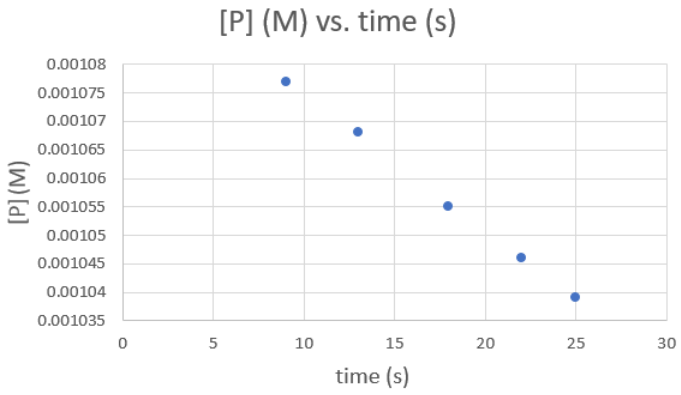
Time (h)	0	2.0×10^3	7.6×10^3	1.23×10^4	1.70×10^4	1.70×10^4
$[O_3]$ (*M*)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}

Solution

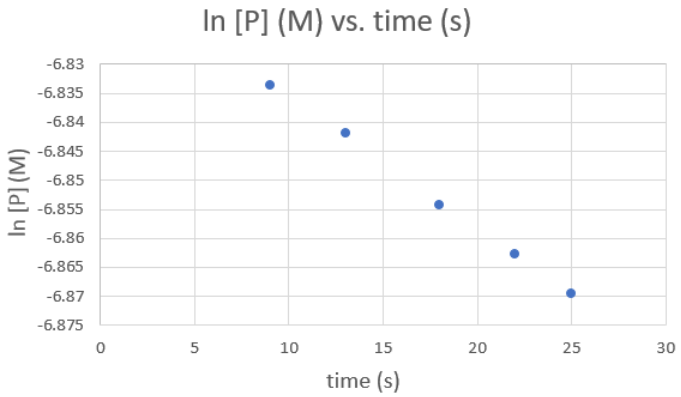
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To determine the order and rate constant, you need to graph the data for zero order, first order, and second order by plotting concentration versus time- [A] vs. time, natural logarithm (ln) of [A] vs. time, and 1/[A] vs. time respectively. The order of the reaction is determined by identifying which of these three graphs produces a straight line. The rate constant *k* is represented by the slope of the graph. The graphs with their respective data values would be

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077 × 10−3	1.068 × 10−3	1.055 × 10−3	1.046 × 10−3	1.039 × 10−3

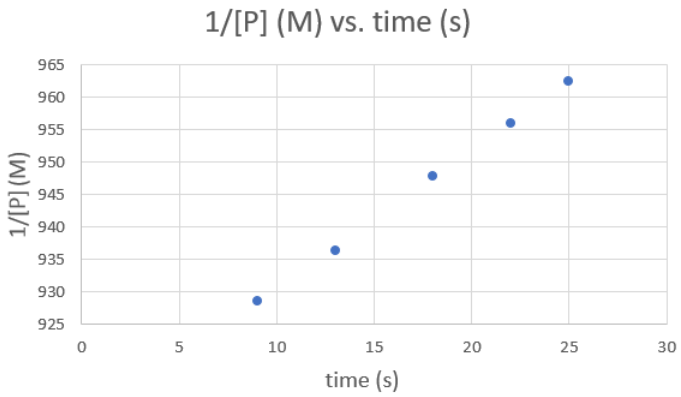


Time (s)	9.0	13.0	18.0	22.0	25.0
ln [P] (*M*)	-6.83358	-6.84197	-6.85421	-6.86278	-6.8695



Time (s)	9.0	13.0	18.0	22.0	25.0
1/[P] (*M*)	928.5051	936.3296	947.8673	956.0229	962.4639

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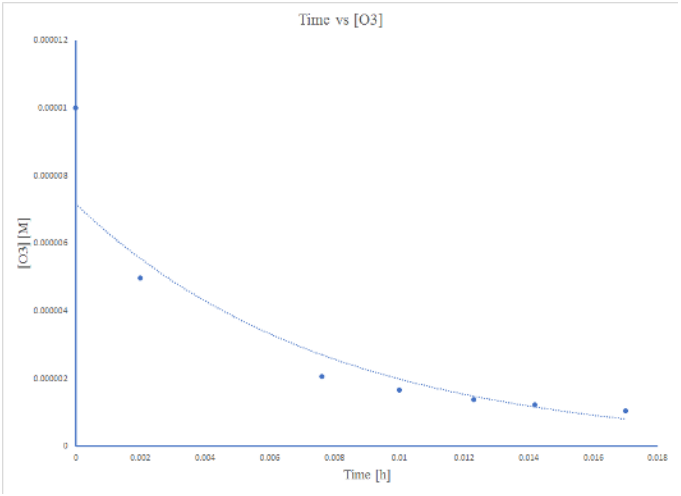
Since each graph yields a straight line **the order and rate constant of the reaction cannot be determined**.

To identify how the concentrations changes a function of time, requires solving the appropriate differential equation (i.e., the differential rate law).

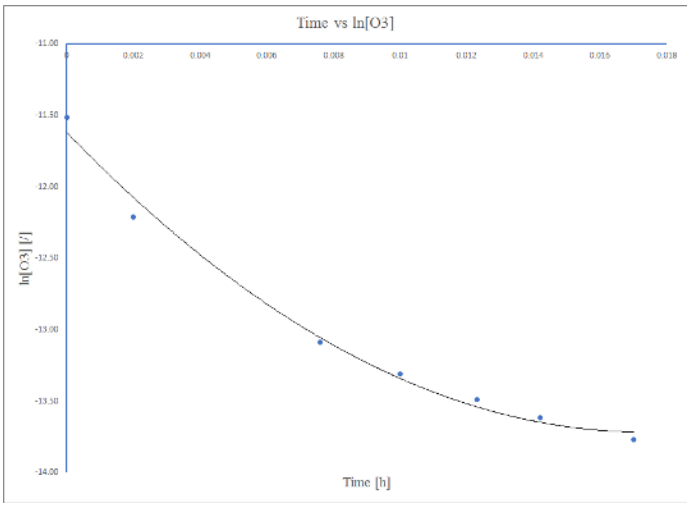
The zero-order rate law predicts in a linear decay of concentration with time

The 1st-order rate law predicts in an exponential decay of concentration with time

The 2nd-order rate law predicts in an reciprocal decay of concentration with time

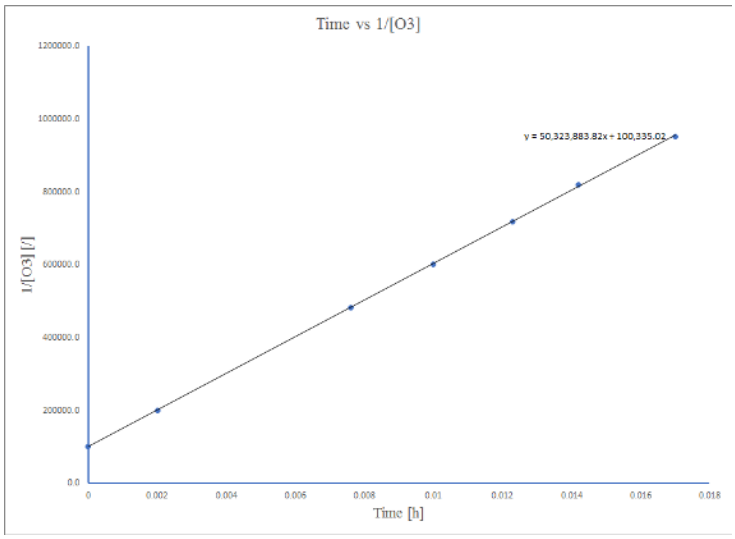


The plot is not linear, so the reaction is not zero order.



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The plot is not linear, so the reaction is not first order.



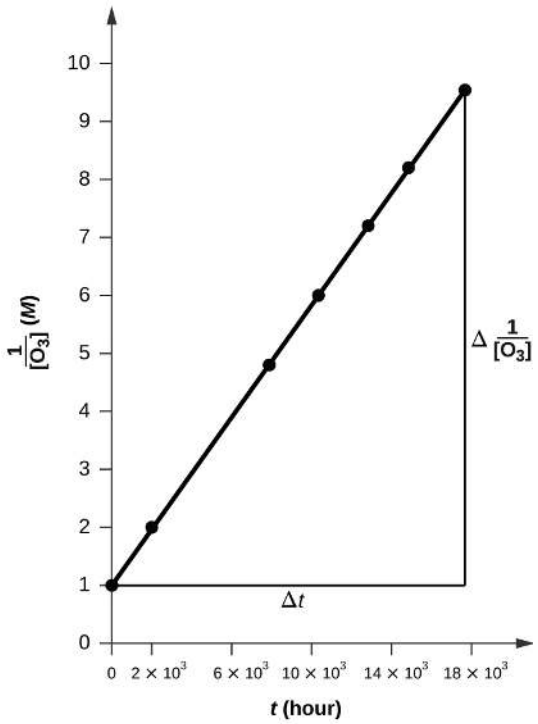
The plot is nicely linear, so the reaction is second order.

To a second order equation, $1/[A] = k*t+1/[A_0]$

Thus, the value of K is the slope of the graph Time vs $\frac{1}{O_3}$,

k = 50.3*10^6 L mol^{-1} h^{-1}

Answer



The plot is nicely linear, so the reaction is second order.

k = 50.1 L mol^{-1} h^{-1}

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Q12.4.5

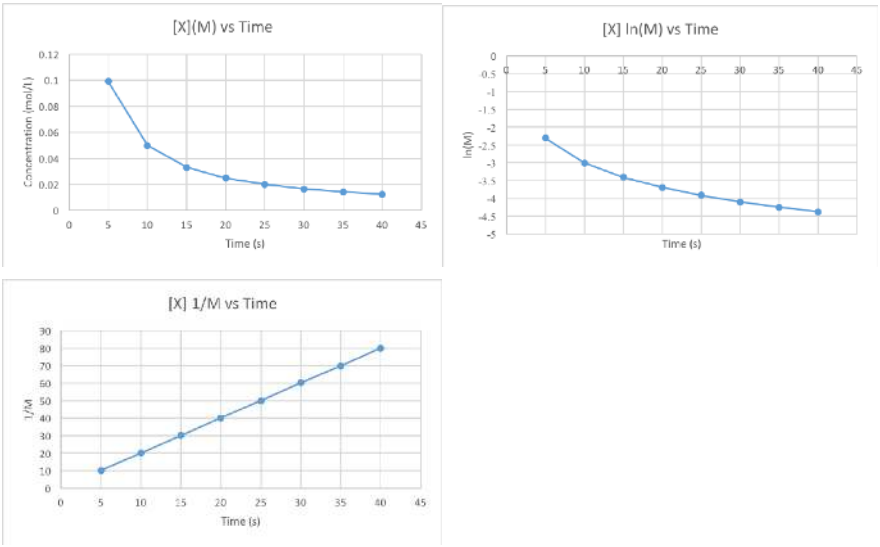
From the given data, use a graphical method to determine the order and rate constant of the following reaction:

$$2X \longrightarrow Y + Z \tag{1.E.13}$$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[X] (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Solution

In order to determine the order of the reaction we need to plot the data using three different graphs. All three graphs will have time in seconds as the x-axis, but the y-axis is what will differ. One graph will plot concentration versus time, the second will plot natural log of concentration versus time, and the other will plot 1/concentration versus times. Whichever graph results in a line, we know that must be the order of the reaction. If we get a line using the first graph, it will be zero order, if it is a line for the second graph it will be first order, and if it is a line for the third graph it will be a second order reaction. Now lets plot the data to determine the order.



We can clearly see that the third graph, which plots 1/M versus time, is a straight line while the other two are slightly curved. Therefore, we can determine that the rate of this reaction is second order. This also tells us that the units of the rate constant which should be $M^{-2}s^{-1}$ for a second order reaction.

To determine the rate constant, called k, we simple need to figure out the slope of the third graph since that is the order of this reaction. To find the slope of the line, we take two points and subtract the y values and then divide them by the difference of the x values. This is how to do it:

Use the points (5, 10.101) and (40, 80).

Now use these to get the slop, aka the rate constant: (80-10.101)/(40-5) = 1.997 = k

So the rate constant for this second order reaction is 1.997 $M^{-1}s^{-1}$.

Q12.4.6

What is the half-life for the first-order decay of phosphorus-32? ($^{32}_{15}\mathrm{P} \longrightarrow {}^{32}_{16}\mathrm{S} + \mathrm{e}^-$) The rate constant for the decay is 4.85×10^{-2} day^{-1}.

Solution

This is a first order reaction, so we can use our half life equation below:

$$t_{1/2} = \frac{0.693}{k}$$

The rate constant is given to us in units per day. All we have to do, is to plug it into the equation.

$$t_{1/2} = \frac{0.693}{4.85 * 10^{-2}}$$

$$= 14.3\ days$$

A12.4.6

14.3 d

Q12.4.7

What is the half-life for the first-order decay of carbon-14? ($^{6}_{14}C \longrightarrow {}^{7}_{14}N + e^{-}$) The rate constant for the decay is 1.21 × 10^{-4} $year^{-1}$.

Solution

To find the half life, we need to use the first-order half-life equation. All half life reactions undergo first order reactions.

The half-life equation for first order is

$$t_{1/2} = ln2/k$$

with k being the rate constant. The rate constant for carbon-14 was given as $1.21 \times 10^{-4} year^{-1}$.

Plug it in the equation.

$$t_{1/2} = ln2/(1.21 \times 10^{-4} year^{-1})$$

and solve for $t_{1/2}$.

When you calculate it, the half life for carbon-14 is 5.73*10^{3}

Answer

The half-life for carbon-14 is calculated to be 5.73*10^{3}

Q12.4.8

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0 × 10^{-8} L/mol/s.

Solution

The half-life of a reaction, $t_{1/2}$, is the amount of time that is required for a reactant concentration to decrease by half compared to its initial concentration. When solving for the half-life of a reaction, we should first consider the order of reaction to determine it's rate law. In this case, we are told that this reaction is second-order, so we know that the integrated rate law is given as:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_{0}}$$

Isolating for time, we find that:

$$t_{1/2} = \frac{1}{k[A]_{0}}$$

Now it is just a matter of substituting the information we have been given to calculate $t_{1/2}$, where the rate constant, k, is equal to 8.0 × 10^{-8} L/mol/s and initial concentration, $[A]_0$, is equal to 0.15*M*:

$$t_{1/2} = \frac{1}{(8.0 \times 10^{-8})(0.15)} = 8.33 \times 10^{7} seconds$$

Answer

8.33×10^7 s

Q12.4.9

What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L/mol/h.

Solution

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Since the reaction is second order, its half-life is

$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$$

$$t_{1/2} = \frac{1}{(50.4 M^{-1}/h)[2.35 \times 10^{-6} M]}$$

So, half-life is 8443 hours.

Q12.4.10

The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L/mol/s. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution

As mentioned in the question the reaction of compound *A* will result in the formation of compounds C and D. This reaction was found to be second-order in *A*. Therefore, we should use the second order equation for half-life which relates the rate constant and initial concentrations to the half-life:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Since we were given *k* (rate constant) and Initial concentration of A, we have everything needed to calculate the half life of A.

$$k = 0.5 \frac{\frac{L}{mol}}{s}$$

$$[A]_0 = 2.42 \frac{mol}{L}$$

When we plug in the given information notice that the units cancel out to seconds.

$$t_{\frac{1}{2}} = \frac{1}{\frac{2.42 L mol^-}{s}[0.500 \frac{mol}{L}]} = 0.826 s$$

Answer

0.826 s

Q12.4.11

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 minutes when the initial concentration of *A* is 0.150 mol/L. How long will it take for the concentration to drop to 0.0300 mol/L if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

Solution

Organize the given variables:

(half-life of A) $t_{1/2} = 8.50min$
(initial concentration of A) $[A]_0 = 0.150mol/L$
(target concentration of A) $[A] = 0.0300mol/L$

Find the the rate constant k, using the half-life formulas for each respective order. After finding k, use the integrated rate law respective to each order and the initial and target concentrations of A to find the time it took for the concentration to drop.

(a) first order with respect to A

(half-life) $t_{1/2} = \frac{ln(2)}{k} = \frac{0.693}{k}$
(rearranged for k) $k = \frac{0.693}{t_{1/2}}$
(plug in $t_{1/2}$ = 8.50 min) $k = \frac{0.693}{8.50min} = 0.0815min^{-1}$

(integrated rate law) $ln[A] = -kt + ln[A]_0$
(rearranged for t) $ln(\frac{[A]}{[A]_0}) = -kt$
$-ln(\frac{[A]}{[A]_0}) = kt$
$ln(\frac{[A]}{[A]_0})^{-1} = kt$
$ln(\frac{[A]_0}{[A]}) = kt$
$t = \frac{ln(\frac{[A]_0}{[A]})}{k}$
(plug in variables) $t = \frac{ln(\frac{0.150mol/L}{0.0300mol/L})}{0.0815min^{-1}} = \frac{ln(5.00)}{0.0815min^{-1}} = 19.7min$

(b) second order with respect to A

(half-life) $t_{1/2} = \frac{1}{k[A]_0}$
(rearranged for k) $k = \frac{1}{t_{1/2}[A]_0}$
(plug in variables) $k = \frac{1}{(8.50min)(0.150mol/L)} = \frac{1}{1.275min \cdot mol/L} = 0.784L/mol \cdot min$

(integrated rate law) $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
(rearranged for t) $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
$t = \frac{1}{k}(\frac{1}{[A]} - \frac{1}{[A]_0})$
(plug in variables) $t = \frac{1}{0.784L/mol \cdot min}(\frac{1}{0.0300mol/L} - \frac{1}{0.150mol/L}) = \frac{1}{0.784L/mol \cdot min}(\frac{80}{3}L/mol) = 34.0min$

Answer

a) 19.7 min

b) 34.0 min

Q12.4.12

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3 × 10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate equation that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15 × 10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (M)	Rate (mol/L/min)
2.0 × 10^{-6}	1.0 × 10^{-10}
3.0 × 10^{-6}	1.5 × 10^{-10}
4.0 × 10^{-6}	2.0 × 10^{-10}

Solution

The first step is to solve for the order or the reaction. This can be done by setting up two expressions which equate the rate to the rate constant times the molar concentration of penicillin raised to the power of it's order. Once we have both expressions set

up, we can divide them to cancel out k (rate constant) and use a basic logarithm to solve for the exponent, which is the order. It will look like this.

$$\text{rate(mol/L/min)}=k[M]^x$$

$$(1.0 \times 10^{-10})=k[2.0 \times 10^{-6}]^x$$

$$(1.5 \times 10^{-10})=k[3.0 \times 10^{-6}]^x$$

Dividing the two equations results in the expression:

$$(2/3)=(2/3)^x$$

*A single ratio equation can also be set up to solve for the reaction order:

*

$$\frac{rate_1}{rate_2} = \frac{k[Penicillin]_1^x}{k[Penicillin]_2^x}$$

*We then solve for x in a similar fashion.

*

$$\frac{1.0x10^{-10}}{1.5x10^{-10}} = \frac{[2.0x10^{-6}]^x}{[3.0x10^{-6}]^x}$$

We can now use the natural logarithm to solve for x, or simply and intuitively see that in order for the equation to work, **x must be equal to one. Thus, the reaction is of the first order.**

Now that we have the order of the reaction, we can proceed to solve for the value of the rate constant. Substituting x=1 into our first equation yields the expression:

$$(1 \times 10^{-10})=k[2.0 \times 10^{-6}]^1$$

$$k=(1 \times 10^{-10})/(2 \times 10^{-6})$$

$$k= (5 \times 10^{-5}) \text{ min}^{-1}$$

We have a unit of min^{-1} because we divided (mol/L/min) by molarity, which is in (mol/L), yielding a unit of min^{-1}.

We were given two important pieces of information to finish the problem. It is stated that the enzyme has a molecular weight of 3×10^4 g/mol, and that we have a one liter solution that contains (0.15×10^{-6}) g) of penicillinase. Dividing the amount of grams by the molecular weight yields **5×10^{-12} moles**.

$$(0.15 \times 10^{-6}) \text{ g} / (3 \times 10^4) \text{ g/mol} = (5 \times 10^{-12}) \text{ mol}$$

Now that we have the amount of moles, we can divide our rate constant by this value.

$$(5 \times 10^{-5}) \text{ min}^{-1} / (5 \times 10^{-12}) \text{ mol} = \mathbf{(1 \times 10^7) \text{ mol}^{-1} \text{ min}^{-1}}$$

Answer

The reaction is first order with $k = 1.0 \times 10^7 \text{ mol}^{-1} \text{ min}^{-1}$

Q12.4.13

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Solution

This problem is asking us for the percentage of radioactivity remaining after a certain time for both isotopes after 48 hours. We must identify an equation that will help us solve this and we can determine that we can determine this information using the first order equation.

This equation $Ln(N/N_o)$= -kt tells that the Natural log of the fraction remaining is equal to the rate constant times time. To determine the rate constant, we can also compute .693 over the half-life given in the information.

For Technetium-99 we can determine the rate constant by plugging into the second equation: .693/6 hrs= .1155 h^{-1}

Now that we have the rate constant we can plug in : $Ln(N/N_o)=-(.1155h^{-1})(48h)$ so $Ln(N/N_o)=-5.544$ and if we take the inverse of the natural log, we get $(N/N_o)=3.9x10^{-3}$ and if we multiply this by 100, we get .39% remaining.

We can do this same process for Thallium-201 and plugin: .693/73 hrs= .009493151 h^{-1} and when we plug this into the first order equation we get:

$Ln(N/N_o)=-(.009493h^{-1})(48h)$ so $Ln(N/N_o)=-.45567248$ and when we take the inverse of the natural log, we get $(N/N_o)=.6340$ and when multiplied by 100, we get 63.40% remaining which makes sense since its half-life is 73 hours and only 48 hours have passed, half of the amount has yet to be consumed.

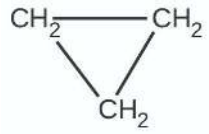
Answer

Technetium-99: 0.39%

Thallium-201: 63.40%

Q12.4.14

There are two molecules with the formula C_3H_6. Propene, $\mathbf{CH_3CH{=}CH_2}$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of 5.95×10^{-4} s^{-1}. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution

Use the equation

$$t_{1/2} = \frac{ln2}{k}$$

since this is a first-order reaction. You can tell that this is a **first order reaction** due to the units of measurement of the rate constant, which is s^{-1}. Different orders of reactions lead to different rate constants, and a rate constant of s^{-1} will always be first order.

Plug into the equation, and you get half life = 1164.95 seconds. To convert this to hours, we would divide this number by 3600 seconds/hour, to get **0.324 hours**.

Use the integrated first order rate law

$$ln\frac{[A]}{[A]_0} = -kt$$

. In this equation, $[A]_0$ represents the initial amount of compound present at time 0, while [A] represents the amount of compound that is left after the reaction has occurred. Therefore, the fraction

$$\frac{[A]}{[A]_0}$$

is equal to the fraction of cyclopropane that remains after a certain amount of time, in this case, 0.75 hours.

Substitute x for the fraction of

$$\frac{[A]}{[A]_0}$$

into the integrated rate law:

$$ln\frac{[A]}{[A]_0} = -kt$$

$$ln(x) = -5.95x10^{-4}(0.75)$$

$$x = e^{(-0.000595)(0.75)}$$

= 0.20058 = 20%.

So, the half life is 0.324 hours, and 20% of the cyclopropane will remain as 80% will have formed propene.

Answer

0.324 hours. ; 20% remains

Q12.4.16

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the nuclear equation is $^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{1}\mathrm{e}^{+}$.) Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

a. What is the rate constant for the decomposition of fluorine-18?
b. If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?
c. How long does it takFe for 99.99% of the ^{18}F to decay?

Solution

a) The nuclear decay of an isotope of an element is represented by the first order equation:

$$\ln(N/N0) = -kt$$

Where t is time, N0 is the initial amount of the substance, N is the amount of the substance after time t, and k is the rate constant. We can rearrange the equation and isolate k so that we could solve for the rate constant:

$$k = [-\ln(N/N0)] / t$$

We are given that fluorine-18 has a half-life of 109.7 minutes. Since we have the half-life, we can choose an arbitrary value for N_0 and use half of that value for N. In this case, we choose 100 for N_0 and 50 for N. Now we can plug in those values into the equation above and solve for k.

$$k = [-\ln(50/100)] / 109.7$$

$$k = 0.6931 / 109.7 = 0.006319\ \mathrm{min}^{-1}$$

The rate constant for this reaction is 0.006319 min^{-1}.

b) For this problem, we are able to use the same equation from part a:

$$\ln(N/N0) = -kt$$

However, this time we are given the amount of time elapsed instead of the half-life, and we are asked to determine the percent of fluorine-18 radioactivity remaining after that time. In this problem, we must plug in values for N0, k (determined from part a), and t.

But first, since we are given the elapsed time in hours, we must convert it into minutes:

$$5.59\ \text{hours} \times (60\ \text{minutes} / 1\ \text{hours}) = 335.4\ \text{minutes}$$

This gives us the value for t. We also have values for k (0.006319 min^{-1}) and N_0 (again an arbitrary number.) Now we can plug values into the original equation, giving us:

$$\ln(N/100) = -(0.006319)(335.4)$$

We solve this equation by taking the exponential of both sides:

$$e^{\ln(N/100)} = e^{-(0.006319)(335.4)}$$

where e^{ln} equals 1 and now we can just solve for N:

$$N/100 = e^{-(0.006319)(335.4)}$$

$$N = [e^{-(0.006319)(335.4)}] \times 100 = 12.0$$

Since 100 was used as the initial amount and 12.0 was determined as the remaining amount, 12.0 can be used as the percentage of remaining amount of radioactivity of fluorine-18. **Thus the percent of fluorine-18 radioactivity remaining after 5.59 hours is 12.0%.**

c) This part of the question is much like the previous two parts, but this time we are given the initial amount of radioactivity, the final amount of radioactivity and we are asked do determine how long it took for that amount of radioactivity to decay. We are able to use the same equation:

$$\ln(N/N0) = -kt$$

However, now we are given N and N_0 and we have already determined k from before. We are told that 99.99% of the radioactivity has decayed, so we can use 100 and 0.01 for N_0 and N respectively. We plug these values in to the equation, solve for t, and get

$$\ln(0.01/1000) = -0.006319t$$

$$-9.21 = -0.006319t$$

$$t = 1458 \text{ minutes}$$

Therefore, its takes 1458 minutes for 99.99% of the radioactivity to decay.

Answer

a) 0.006319 min^{-1}

b) 12.0%

c) 1458 minutes

Q12.4.17

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

Solution

252 days

for first order reaction: $t_{1/2} = 0.693 / k$

$k = 0.693 / 42$

$k = 0.0165$

for first order reaction: $[A] = [A]_0 e^{-kt}$

1/64 initial means that: $[A] = 1/64 [A]_0$

therefore: $1/64 [A]_0 = [A]_0 e^{-0.0165t}$

$t = 252$ days

Q12.4.18

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Solution

In order to find out what year King Richard III died, set [A]/[A_0] (the percent of carbon-14 still contained) equal to $0.5^{\text{time(t)/half life } (t_{1/2})}$ or use the equation $N(t) = N_0e^{-rt.}$

Using the first equation:

$A/A_0 = 0.5^{t/t_{1/2}}$ plug in the given numbers $.9379 = 0.5^{t/5730}$ and solve for t.

$ln.9379 = (t/5730)(ln0.5)$ (using the rule of logs)

$-.0641 = (t/5730)(-.693)$

$-367.36 = -.693t$

$t = 530.1 years$

Using $N(t) = N_0e^{-rt}$ this problem is solved by the following:

$1/2 = e^{-5730r}$

$r = 0.000121$

Now that we know what r is, we can use this value in our original formula and solve for t, the amount of years that have passed.

This time, we use 93.78, the percent of the carbon-14 remaining as N(t) and 100 as the original, N_0.

$93.78 = 100e^{-0.000121t}$

$t = 530.7$ years

Another way of doing this is by using these two equations:

$\lambda = \frac{0.693}{t_{1/2}}$ and $\frac{n_t}{n_0} = -\lambda t$

n_t = concentration at time t (93.79)

n_0 = initial concentration (100)

First solve for lambda or the decay constant by plugging in the half life.

Then plug in lambda and the other numbers into the second equation, and solve for t- which should equal to 530.1 years as well.

If we want to find out what year King Richard III died, we take the current year, 2017, and subtract 530 years. Doing this, we find that King Richard III died in the year 1487.

Answer

King Richard III died in the year 1487

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Q12.4.19

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution

First we need to understand what the question is asking for: the average rate constant. The average rate constant is the variable "k" when discussing kinetics and it can be defined as the proportionality constant in the equation that expresses the relationship between the rate of a chemical reaction and the concentrations of the reacting substances. Knowing that we need to find K in this first order reaction, we can look to formulas that include "k," initial and final concentrations $[A]_o and [A]_t$, and half life time "t." Since this is a first order reaction, we can look to the first order equations, and doing that we find one that includes the variables given in the question:

$$\ln [A]_t = -kt + \ln [A]_o$$

For the first reaction, we have an initial concentration of 4.88 M, and a percentage decomposed. To find the final concentration, we must multiply the initial concentration by the percentage decomposed to know how much decomposed, and subtract that from the original to find out how much is left: 4.88M x 0.52= 2.54 M and 4.88M-2.54M=2.34M

Now, we have the variables we need, and we plug it into the equation above:

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[2.34M] = -k(300s) + \ln[4.88M]$

k= $\frac{-(\ln[2.34M]-\ln[4.88M])}{300}$

$k = 2.45x10^{-3}$

Since it asks for the rate constant of each experiment, we now must do the same procedure for each data set to find the rate constant:

Second experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.66M] = -k(300s) + \ln[3.52M]$

k= $\frac{-(\ln[1.66M]-\ln[3.52M])}{300}$

$k = 2.51x10^{-3}$

Third experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.07M] = -k(300s) + \ln[2.29M]$

k= $\frac{-(\ln[1.07M]-\ln[2.29M])}{300}$

$k = 2.54x10^{-3}$

Fourth experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[0.834M] = -k(300s) + \ln[1.81M]$

$k = \frac{-(\ln[0.834M] - \ln[1.81M])}{300}$

$k = 2.58x10^{-3}$

Fifth Experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[3.49M] = -k(180s) + \ln[5.33M]$

$k = \frac{-(\ln[3.49M] - \ln[5.33M])}{180}$

$k = 2.35x10^{-3}$

Sixth Experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[2.60M] = -k(180s) + \ln[4.05M]$

$k = \frac{-(\ln[2.60M] - \ln[4.05M])}{180}$

$k = 2.46x10^{-3}$

Seventh Experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.89M] = -k(180s) + \ln[2.95M]$

$k = \frac{-(\ln[1.89M] - \ln[2.95M])}{180}$

$k = 2.47x10^{-3}$

Eighth experiment

$\ln [A]_t = -kt + \ln [A]_o$

$\ln[1.11M] = -k(180s) + \ln[1.72M]$

$k = \frac{-(\ln[1.11M] - \ln[1.72M])}{180}$

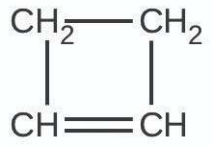
$k = 2.43x10^{-3}$

Answer

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.54
1.81	2.58
5.33	2.35
4.05	2.44
2.95	2.47
1.72	2.43

Q12.4.20

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene ($\mathbf{CH_2{=}CH{-}CH{=}CH_2}$) has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0×10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

Solution

Since this is a first order reaction, the integrated rate law is: $[A_t] = [A_0]e^{-kt}$

Partial Pressure: Use the integrated rate law to find the partial pressure at 30 minutes:

Use A_0 = 55 torr, t = 30 min, and k = $2.0 * 10^{-4} s^{-1}$ to solve the integrated rate law equation:

$[A_{30}] = (55torr) * e^{-(2.0x10^{-4}\frac{1}{sec})(30min \cdot \frac{60sec}{1min})}$

Solve this equation to get:

$[A_{30}] = (55torr) * e^{-0.36}$

$A_{30}]$ = 38.37 torr.

Initial Concentration: Find the initial concentration using the ideal gas law.

The ideal gas law is given by $PV = nRT \rightarrow n = \frac{PV}{RT}$. Use this form of the gas law to solve for the initial concentration n.

Use V = 0.53L, R = 0.08206 $\frac{L*atm}{mol*L}$, T = 423.15 K, and P = $\frac{1atm}{760}$ = 0.07237 atm .

Solve the ideal gas equation using these values:

$n = \frac{(55torr)(0.53L)}{(0.08206\frac{L*atm}{mol*K})(423.15K)} = 0.00110$ moles cyclobutene.

Now find the initial concentration of cyclobutene A_0 using the equation $[A_0] = \frac{n}{V}$:

$A_0 = \frac{n}{V} = \frac{0.00110moles}{0.53L} = 0.00208M$

Concentration at 30 minutes: Find the concentration of cyclobutene at 30 minutes by using the integrated rate law given above, using time t = 30 minutes, or 1800 seconds.

$[A_{30}] = (0.00208M)e^{-0.36} = 0.00145M$

So at 30 minutes, the cyclobutene concentration is 0.00145 M, and the partial pressure is 38.37 torr.

Answer

Partial Pressure: 38.37 torr.

Concentration: 0.00145 M

12.5: Collision Theory

Q12.5.1

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution

The two factors that may prevent a collision from producing a chemical reaction are:

1. **Kinetic energy of the molecule**

In order for chemical reactions to occur, molecules require enough velocity to overcome the minimum activation energy needed to break the old bonds and form new bonds with other molecules. At higher temperatures, the molecules possess the minimum amount of kinetic energy needed which ensures the collisions will be energetic enough to lead to a reaction.

2. **The orientation of molecules during the collision**

Two molecules have to collide in the right orientation in order for the reaction to occur. Molecules have to orient properly for another molecule to collide at the right activation state.

Q12.5.2

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

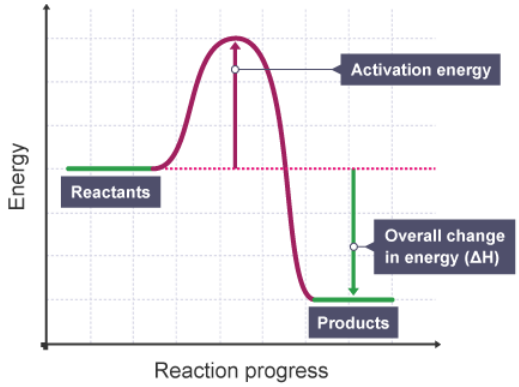
Solution

There has to be contact between reactants for a reaction to occur. The more the reactants collide, the more often reactions can occur. Factors that determine reaction rates include concentration of reactants, temperature, physical states of reactants, surface area, and the use of a catalyst. The reaction rate usually increases as the concentration of a reactant increases. Increasing the temperature increases the average kinetic energy of molecules, causing them to collide more frequently, which increases the reaction rate. When two reactants are in the same fluid phase, their particles collide more frequently, which increases the reaction rate. If the surface area of a reactant is increased, more particles are exposed to the other reactant therefore more collisions occur and the rate of reaction increases. A catalyst participates in a chemical reaction and increases the reaction rate without changing itself.

Q12.5.3

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution



Activation energy is the energy barrier that must be overcome in order for a reaction to occur. To get the molecules into a state that allows them to break and form bonds, the molecules must be contorted (deformed, or bent) into an unstable state called the transition state. The transition state is a high-energy state, and some amount of energy – the activation energy – must be added in order for the molecule reach it. Because the transition state is unstable, reactant molecules don't stay there long, but quickly proceed to the next step of the chemical reaction.The activated complex is the highest energy of the transition state of the reaction.

Q12.5.5

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Solution

This method is based on the **Arrhenius equation** which can be used to show the effect of a change of temperature on the **rate constant**, and therefore on the rate of reaction.

The rate constant is different from reaction rat in that the reaction rate is the measure of how fast or slow a chemical reaction takes place while a rate constant is a constant that shows the relationship between the reaction rate and the concentrations of the reactants or products.

For example, for the reaction $A + B \rightarrow C$, the rate law would be:

$$rate = k[A]^a[B]^b$$

k = rate constant

[A] = concentration of reactant A

a = order of reaction with respect to A

[B] = concentration of reactant B

b = order of reaction with respect to B

However, the rate constant remains constant only if you are changing the concentration of the reactants. If you change the temperature or the catalyst of the reaction, the rate constant will change and this is demonstrated by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$ln\left(\frac{k_1}{k_2}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

k = rate constant

A = frequency factor

E_a = activation energy

e = exponential function, e^x

R = gas constant

T = temperature (K)

In other words, the activation energy of a reaction, E_a, from a series of data that includes the rate of reaction, k, at varying temperatures can be determined by graphing it on a plot of $\ln k$ versus $\frac{1}{T}$. You can then use the slope of the graph you have plotted to solve for E_a by setting the slope equal to $\frac{-E_a}{R}$.

Q12.5.6

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

S12.5.6

Collision theory states that the rates of chemical reactions depend on the fraction of molecules with the correct orientation, fraction of collisions with required energy, and the collision frequency. Because the fraction of collisions with required energy is a function of temperature, as temperature increases, the fraction of collisions with required energy also increases. The kinetic energy of reactants also increases with temperature which means molecules will collide more often increasing collisions frequency. With increased fraction of collisions with required energy and collisions frequency, the rate of chemical reaction increases. We see mathematically, from the Arrhenius equation, that temperature and the rate constant are related.

$$k = Ae^{\frac{E_a}{RT}} \tag{1.E.14}$$

where k is the rate constant, A is a specific constant, R is 8.3145 J/K, Ea is the reaction-specific activation energy in J, and T is temperature in K. We see from the equation that k is very sensitive to changes in the temperature.

Q12.5.7

The rate of a certain reaction doubles for every 10 °C rise in temperature.

a. How much faster does the reaction proceed at 45 °C than at 25 °C?
b. How much faster does the reaction proceed at 95 °C than at 25 °C?

Solution

By finding the difference in temperature, 45 °C - 25 °C, we get 20 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the rate of the reaction experienced a 20 °C increase in temperature, we see that the reaction rate doubled twice ($2^2 = 4$). As a result, the **reaction proceeds four times faster**.

Following the same process as in part a, we get the difference in temperature to be 70 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the system experienced a 70 °C change, we see that the reaction doubled seven times ($2^7 = 128$). We can see the **reaction proceeds 128 times faster**.

(a) 4-times faster (b) 128-times faster

Q12.5.8

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher?

S12.5.8

First off, it is important to recognize that this decomposition reaction is a **first-order reaction**, which can be written as follows: $2NaClO_3 \rightarrow 2NaCl + 3O_2$

Understanding this, it is important to be able to then be able to recognize which equation would be most useful given the initial conditions presented by the question. Since we are dealing with time, percentage of material left, and temperature, the only viable equation that could relate all of this would be the Arrhenius Equation, which is written as follows: $\ln(\frac{k_2}{k_1}) = \frac{Ea}{R}(\frac{1}{t_1} - \frac{1}{t_2})$

However, this problem does not give us enough information such as what the activation energy is or the initial temperature in order to mathematically solve this problem. Additionally, the problem tells us to approximate how long the decomposition would take, which means we are asked to answer this question conceptually based on our knowledge of thermodynamics and reaction rates. As a general rule of thumb, we know that for every 10˚C rise in temperature the rate of reaction doubles. Since the question tells us that there is a 20˚C rise in temperature we can deduce that the reaction rate doubles twice, as per the general rule mentioned before. This means **the overall reaction rate for this decomposition would quadruple**, or would be 4 times faster than the reaction rate at the initial temperature.

We can gut check this answer by recalling how an increase in the average kinetic energy (temperature) decreases the time it takes for the reaction to take place and increase the reaction rate. Thus, if we increase the temperature we should have a faster reaction rate.

Q12.5.9

The rate constant at 325 °C for the decomposition reaction $C_4H_8 \longrightarrow 2\,C_2H_4$ is 6.1×10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

Solution

S12.5.9

Using the Arrhenius equation allows me to find the frequency factor, A.

$k=Ae^{-Ea/RT}$

k, Ea, R, and T are all known values. k, Ea, and T are given in the problem as $6.1x10^{-8}$, 261 kJ, and 598 K, respectively.

So, plugging them into the equation gives:

$6.1x10^{-8}\ s^{-1}=Ae^{(-261000\ J)/(8.3145\ J/mol)(598\ K)}$

Take $e^{(-261000\ J)/(8.3145\ J/mol)(598)}$ and get 1.59×10^{-23}. Divide k, 6.1×10^{-8}, by 1.59×10^{-23} and get A=$3.9 \times 10^{15} s^{-1}$

A12.5.9

$3.9 \times 10^{15}\ s^{-1}$

Q12.5.10

The rate constant for the decomposition of acetaldehyde (CH_3CHO), to methane (CH_4), and carbon monoxide (CO), in the gas phase is 1.1×10^{-2} L/mol/s at 703 K and 4.95 L/mol/s at 865 K. Determine the activation energy for this decomposition.

S12.5.10

The equation for relating the rate constant and activation energy of a reaction is the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \tag{1.E.15}$$

When given two rate constants at two different temperatures but for the same reaction, the Arrhenius equation can be rewritten as:

$$ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{1.E.16}$$

In this problem, all the variables are given except for the E_a (activation energy).

$k_1 = 1.1 \times 10^{-2}$ L/mol/s

$T_1 = 703$ K

$k_2 = 4.95$ L/mol/s

$T_2 = 865$ K

R = 8.314 J/(mol K) (Ideal Gas Constant)

Now plug in all these values into the equation, and solve for E_a.

$$ln(\frac{4.95 \frac{L}{mol \times s}}{1.1 \times 10^{-2} \frac{L}{mol \times s}}) = \frac{E_a}{8.314 \times 10^{-3} \frac{kJ}{mol \times K}}(\frac{1}{703} - \frac{1}{865}) \tag{1.E.17}$$

$E_a = 190$ kJ (2 sig figs)

Q12.5.11

An elevated level of the enzyme alkaline phosphatase (ALP) in the serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Solution

43.0 kJ/mol

Q12.5.12

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

a. the change in free energy per second
b. the change in temperature per second
c. the number of collisions per second
d. the number of product molecules

Q12.5.13

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, k, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (M^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

Solution

177 kJ/mol

Q12.5.14

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})
293	0.054
298	0.100

Q12.5.15

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$\mathbf{C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6}$$

follows a first-order rate equation for the disappearance of sucrose: Rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

a. In neutral solution, $k = 2.1 \times 10^{-11}$ s^{-1} at 27 °C and 8.5×10^{-11} s^{-1} at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
b. When a solution of sucrose with an initial concentration of 0.150 M reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} M. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.
c. Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution

$E_a = 108$ kJ

$A = 2.0 \times 10^8$ s^{-1}

$k = 3.2 \times 10^{-10}$ s^{-1}

(b) 1.81×10^8 h or 7.6×10^6 day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

Q12.5.16

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

Q12.5.17

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

Solution

The *A* atom has enough energy to react with *BC*; however, the different angles at which it bounces off of *BC* without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

12.6: Reaction Mechanisms

Q12.6.1

Why are elementary reactions involving three or more reactants very uncommon?

Q12.6.2

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution

Add texts here. Do not delete this text first.

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate equation. Yes. If the reaction is an elementary reaction, then doubling the concentration of *A* doubles the rate.

Q12.6.3

Phosgene, $COCl_2$, one of the poison gases used during World War I, is formed from chlorine and carbon monoxide. The mechanism is thought to proceed by:

step 1:	$Cl + CO \rightarrow COCl$
step 2:	$COCl + Cl_2 \rightarrow COCl_2 + Cl$

a. Write the overall reaction equation.
b. Identify any reaction intermediates.
c. Identify any intermediates.

Q12.6.4

Define these terms:

a. unimolecular reaction
b. bimolecular reaction
c. elementary reaction
d. overall reaction

Q12.6.5

What is the rate equation for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution

Add texts here. Do not delete this text first.

We are given that both of these reactions are elementary termolecular. The molecularity of a reaction refers to the number of reactant particles that react together with the proper and energy and orientation. Termolecular reactions have three atoms to collide simultaneously. As it is termolecular, and there are no additional reactants aside from the three given in each reaction, there are no intermediate reactions. The rate law for elementary reactions is determined by the stoichiometry of the reaction without needed experimental data.

The basic rate form for the elementary step is what follows:

$rate = k \cdot reactant\ 1^{i} \cdot reactant\ 2^{ii} \cdot ...$ Where i and ii are the stochiometric coefficient from reactant 1 and 2 respectively.

For: $3A \rightarrow products$

$k \cdot A^3 = rate$

For: $A + 2B \rightarrow products$

$k \cdot [A] \cdot [B]^2 = rate$

Note that the order of these reactions are both three.

Answer

Add texts here. Do not delete this text first.

Rate = $k[A][B]^2$; Rate = $k[A]^3$

Q12.6.6

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a) $Cl_2 + CO \longrightarrow Cl_2CO$

$\text{rate} = k[Cl_2]^{3/2}[CO]$

(b) $PCl_3 + Cl_2 \longrightarrow PCl_5$

$\text{rate} = k[PCl_3][Cl_2]$

(c) $2\,NO + H_2 \longrightarrow N_2 + H_2O$

$\text{rate} = k[NO][H_2]$

(d) $2\,NO + O_2 \longrightarrow 2\,NO_2$

$\text{rate} = k[NO]^2[O_2]$

(e) $NO + O_3 \longrightarrow NO_2 + O_2$

$\text{rate} = k[NO][O_3]$

Solution

Add texts here. Do not delete this text first.

An elementary reaction is a chemical reaction in which the reactants directly form products in a single step. In another words, the rate law for the overall reaction is same as experimentally found rate law. Out of 5 options, option (b),(d), and (e) are such reactions

Q12.6.7

Write the rate equation for each of the following elementary reactions:

a. $O_3 \xrightarrow{sunlight} O_2 + O$
b. $O_3 + Cl \longrightarrow O_2 + ClO$
c. $ClO + O \longrightarrow Cl + O_2$
d. $O_3 + NO \longrightarrow NO_2 + O_2$
e. $NO_2 + O \longrightarrow NO + O_2$

Solution

Add texts here. Do not delete this text first.

Rate equations are **dependent on the reactants and not the products.**

The rate law of a reaction can be found using a rate constant (which is found experimentally), and the initial concentrations of reactants.

A general solution for the equation

$aA + bB \rightarrow cC + dD$

is $rate = k[A]^m[B]^n$ where m and n are reaction orders.

However, reaction orders are found experimentally, and since we do not have experimental data for these reactions, we can disregard that part of the equation.

To find the rate laws, all we have to do is plug the reactants into the rate formula. This is only due to the case that these are elementary reactions. Further reading on elementary reactions can be found on Libre Texts.

a. $O_3 \longrightarrow O_2 + O$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3]$$

b. $O_3 + Cl \longrightarrow O_2 + ClO$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][Cl]$$

c. $ClO + O \longrightarrow Cl + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[ClO][O]$$

d. $O_3 + NO \longrightarrow NO_2 + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][NO]$$

e. $NO_2 + O \longrightarrow NO + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[NO_2][O]$$

Answer

Add texts here. Do not delete this text first.

(a) Rate$_1$ = k[O_3]; (b) Rate$_2$ = k[O_3][Cl]; (c) Rate$_3$ = k[ClO][O]; (d) Rate$_2$ = k[O_3][NO]; (e) Rate$_3$ = k[NO_2][O]

Q12.6.8

Nitrogen(II) oxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$2\,NO + H_2 \longrightarrow N_2 + H_2O_2\ (\text{slow})$$

$$H_2O_2 + H_2 \longrightarrow 2\,H_2O\ (\text{fast})$$

The rate law of the mechanism is determined by the slow step of the reaction. Since the slow step is an elementary step, the rate law can be drawn from the coefficients of the chemical equation. So therefore, the rate law is as follows: rate=k$[NO]^2[H_2]$. Since both NO and H_2 are reactants in the overall reaction (therefore are not intermediates in the reaction), no further steps have to be done to determine the rate law.

Q12.6.9

Consider the reaction

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (occurs under light)

The mechanism is a chain reaction involving Cl atoms and CH_3 radicals. Which of the following steps does not terminate this chain reaction?

a. $CH_3 + Cl \rightarrow CH_3CI$
b. $CH_3 + HCl \rightarrow CH_4 + Cl$
c. $CH_3 + CH_3 \rightarrow C_2H_2$
d. $Cl + Cl \rightarrow Cl_2$

Solution

Add texts here. Do not delete this text first.

Chain reactions involve reactions that create products necessary for more reactions to occur. In this case, a reaction step will continue the chain reaction if a radical is generated. Radicals are highly reactive particles, so more reactions in the chain will take place as long as they are present. The chlorine is considered a free radical as it has an unpaired electron; for this reason it is very reactive and propagates a chain reaction. It does so by taking an electron from a stable molecule and making that molecule reactive, and that molecule goes on to react with stable species, and in that manner a long series of "chain" reactions are initiated. A chlorine radical will continue the chain by completing the following reaction:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The CH_3 generated by this reaction can then react with other species, continuing to propagate the chain reaction.

Option 1 is incorrect because the only species it produces is CH_3Cl, a product in the overall reaction that is unreactive. This terminates the chain reaction because it fails to produce any Cl or CH_3 radicals that are necessary for further propagating the overall reaction.

Option 2 is the correct answer because it produces a Cl radical. This Cl radical can continue the chain by colliding with CH_4 molecules.

Option 3 is incorrect because it fails to produce a radical capable of continuing the chain.

Option 4 is incorrect because it produces Cl_2, a molecule that does not react unless additional light is supplied. Therefore, this step breaks the chain.

Answer

Add texts here. Do not delete this text first.

Answer: Option 2: $CH_3 + HCl \rightarrow CH_4 + Cl$

Q12.6.10

Experiments were conducted to study the rate of the reaction represented by this equation.

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol/L)	Initial Concentration, [H_2] (mol/L)	Initial Rate of Formation of N_2 (mol/L min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

a. Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
b. Write the overall rate law for the reaction.
c. Calculate the value of the rate constant, *k*, for the reaction. Include units.
d. For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.
e. The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \rightleftharpoons H_2O + N_2O$

Step 3: $N_2O + H_2 \rightleftharpoons N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

S12.6.10

1. i) Find the order for [NO] by using experiment 3 and 4 where [H_2] is constant

Notice that [NO] doubles from experiment 3 to 4 and the rate quadruples. So the order for [NO] is **2**

ii) Find the order for [H_2] by using experiment 1 and 2 where [NO] is constant

Notice that [H_2] doubles from experiment 1 to 2 and the rate doubles as well. So the order for [H_2] is **1**

2. Put in the order for each product as the exponents for the corresponding reactant.

$$rate = k[NO]^2[H_2]$$

3. Put in the concentrations and the rate from one of the experiments into the rate law and solve for k. (Here, experiement 1 is used but any of them will work)

$$rate = k[NO]^2[H_2]\ .00018 = k[.006]^2[.001]\ k = 5000M^{-2}s^{-1}$$

4. Plug in values for experiment 2 into the rate law equation and solve for the concentration of NO

$$.00036 = 5000[NO]^2[.001]\ [NO]^2 = 7.2x10^{-5}\ [NO] = .0085M$$

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5. Write the rate laws for each step and then see which matches the rate law we found in question 2. The rate determining step (the slow step) is the one that gives the rate for the overall reaction. Because of this, only those concentrations will influence the overall reaction, contrary to what we would believe if we just looked at the overall reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

$rate = k_1[NO]^2$ This rate law is not the same as the one we calculate in question 2 so this **can not** be the rate determining step

Step 2: $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$

$rate = k_2[N_2O_2][H_2]$

Since N_2O_2 is an intermediate you must replace it in the rate law equation. Intermediates can not be in the rate law because they do not appear in the overall reaction. Here you can take the reverse of equation 1 (k_{-1}) and substitute the other side (the reactants of equation 1) for the intermediate in the rate law equation.

$$rate_1 = rate_{-1}$$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1}}$$

$rate = \frac{k_2k_1[NO]^2[H_2]}{k_{-1}}$

Overall: $rate = k[NO]^2[H_2]$ This **is the same** so it is the rate determining step.

So $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$ is the rate determining step step.

Answer

Add texts here. Do not delete this text first.

(a) NO: 2

$\mathbf{H_2}$: 1

(b) Rate = k $[NO]^2[H_2]$;

(c) $k = 5.0 \times 10^3$ mol^{-2} L^{-2} min^{-1};

(d) 0.0050 mol/L;

(e) Step II is the rate-determining step.

Q12.6.11

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

- $Cl_2(g) \rightleftharpoons 2\,Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
- $CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)
- $COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

a. Write the overall reaction.
b. Identify all intermediates.
c. Write the rate law for each elementary reaction.
d. Write the overall rate law expression.

Solution

Add texts here. Do not delete this text first.

1. To write the overall reaction you have to identify the intermediates and leave them out. The easiest way to do this is to write out all the products and reactants and cross out anything that is on both sides.

$$Cl_2(g) + CO(g) + \cancel{2Cl(g)} + \cancel{COCl(g)} \Rightarrow \cancel{2Cl(g)} + \cancel{COCl(g)} + COCl_2(g)$$

In this you will cross out the 2Cl(g) molecules and the COCl(g). What is left after that is the overall reaction.

$Cl_2(g) + CO(g) \Rightarrow + COCl_2(g)$

2. For part two you will just list the intermediates that you crossed out.

Cl and COCl are intermediates

3. Each rate law will be the rate equal to the rate constant times the concentrations of the reactants

reaction 1

(forward) rate=$k_1[Cl_2]$ (reverse) rate=$k_{-1}[Cl]$

reaction 2

rate=$k_2[CO][Cl]$

Reaction 3

rate=$k_3[COCl][Cl]$

4. The overall rate law is based off the slowest step (step #2), since it is the rate determining step, but Cl is present in that rate law so we have to replace it with an equivalent that does not contain an intermediate. To do this you use the equilibrium since the rates are the same you can set up the rate laws of the forward and reverse equal to each other.

$k_1[Cl_2] = k_{-1}[Cl]$

$[Cl]= k_1[Cl_2]/k_{-1}$

rate=$k_2[CO]k_1[Cl_2]/k_{-1}$

rate=$k^{\circ}[CO][Cl_2]$

Steps to replacing and intermediate

1. Set the forward and reverse reaction equal to each other using separate constants
2. Solve for the intermediate using algebra
3. Plug into the rate determining formula
4. All the k's will be condensed into a K prime constant

12.7: Catalysis

Q12.7.1

Account for the increase in reaction rate brought about by a catalyst.

Q12.7.2

Compare the functions of homogeneous and heterogeneous catalysts.

Q12.7.3

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$\begin{aligned} O_3 &\xrightarrow{sunlight} O_2 + O \\ O_3 + Cl &\longrightarrow O_2 + ClO \\ ClO + O &\longrightarrow Cl + O_2 \end{aligned}$$

a. Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2\,O_3 \longrightarrow 3\,O_2$$

b. Nitric oxide is also involved in the decomposition of ozone by the mechanism:

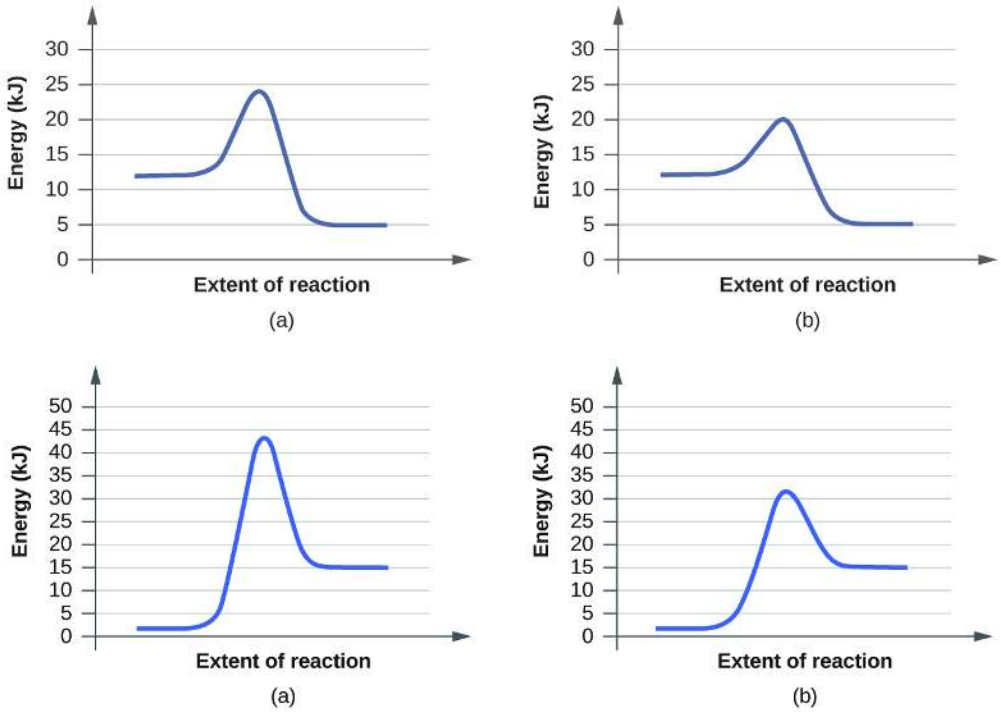
$$O_3 \xrightarrow{sunlight} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

Is NO a catalyst for the decomposition? Explain your answer.

Q12.7.4

For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

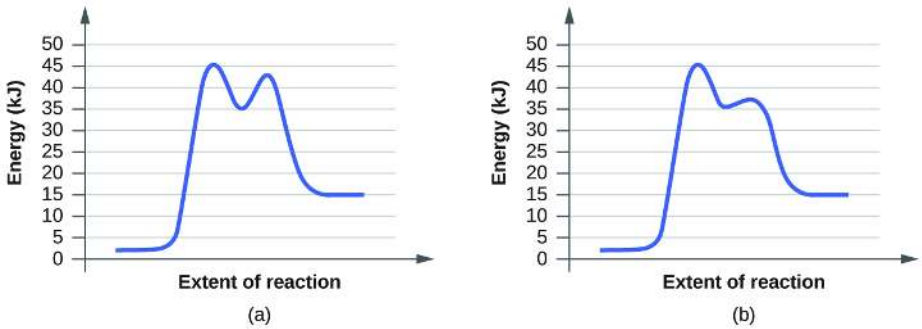
(a)



Q12.7.5

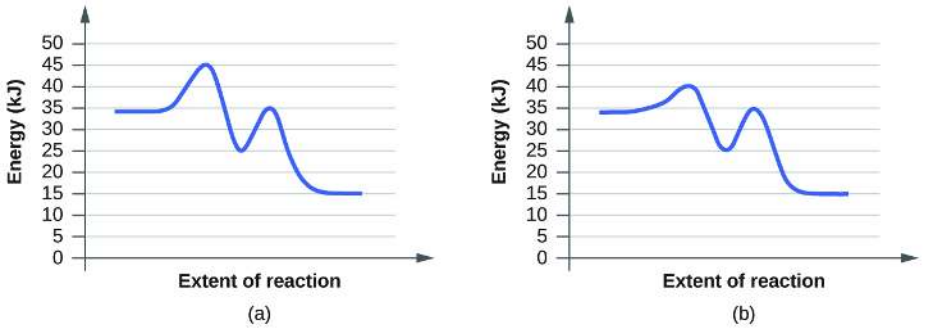
For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)



(b)

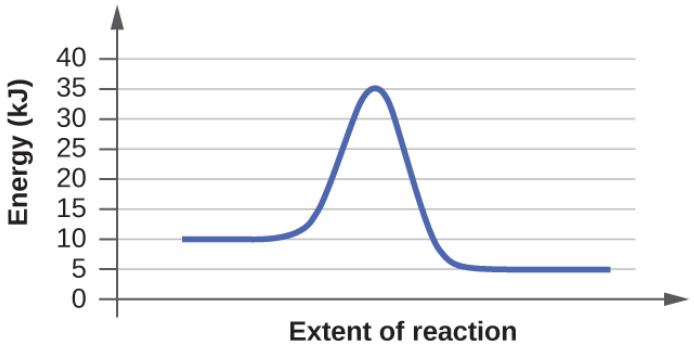
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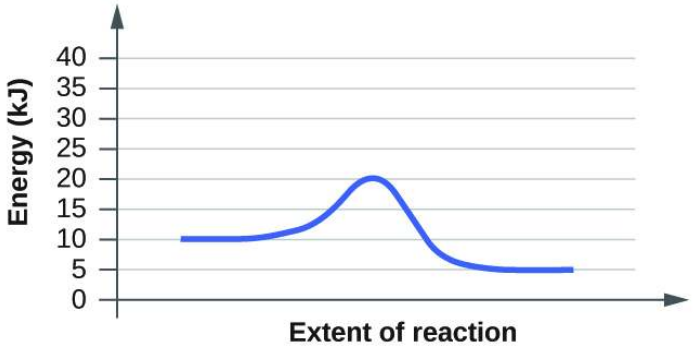
Q12.7.6

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)

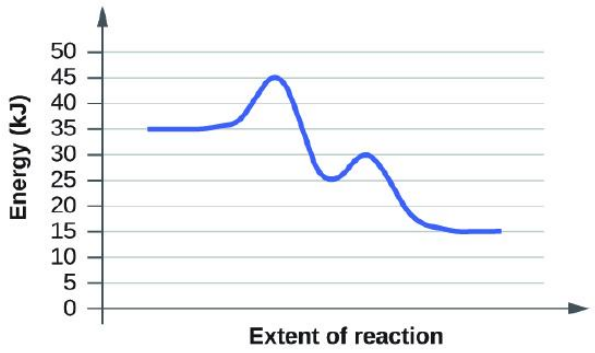


Q12.7.7

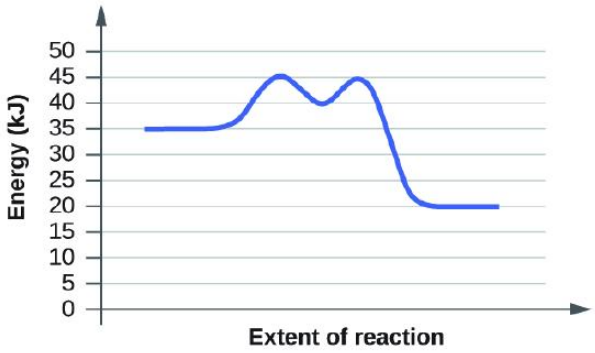
For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)

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(b)



Q12.7.8

1. Based on the diagrams in Question Q12.7.6, which of the reactions has the fastest rate? Which has the slowest rate?
2. Based on the diagrams in Question Q12.7.7, which of the reactions has the fastest rate? Which has the slowest rate?

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CHAPTER OVERVIEW

2: Fundamental Equilibrium Concepts

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General Chemistry

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.

2.1: Prelude to Equilibrium

2.2: Chemical Equilibria

2.3: Equilibrium Constants

2.4: Shifting Equilibria - Le Châtelier’s Principle

2.5: Equilibrium Calculations

2.E: Fundamental Equilibrium Concepts (Exercises)

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2.1: 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.

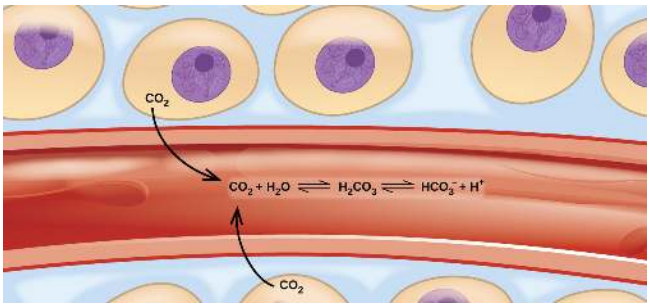


Figure **2.1.1**: Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

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 **2.1.1**). 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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2.2: 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

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{2.2.1}$$

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 2.2.1).

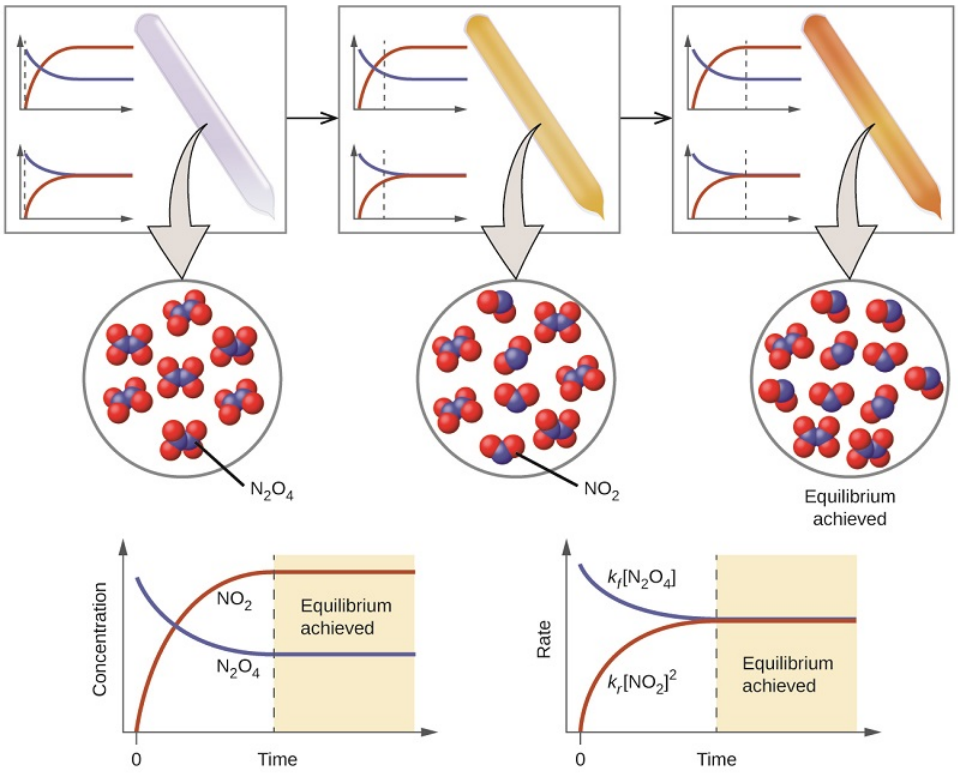


Figure **2.2.1**: A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

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 **2.2.2**).



Figure 2.2.2: 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 2.2.1.

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 2.2.1 shows the reaction:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons \mathrm{2\,NO_2\,(g)} \tag{2.2.2}$$

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 2.2.1, the rate of the forward reaction

$$\mathrm{2\,NO_2\,(g)} \rightarrow \mathrm{N_2O_4\,(g)} \tag{2.2.3}$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4\,(g)} \rightarrow \mathrm{2\,NO_2\,(g)} \tag{2.2.4}$$

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^-).

$$\mathrm{CO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_2CO_3\,(aq)} \rightleftharpoons \mathrm{HCO_3^-\,(aq) + H^+\,(aq)}$$

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 **2.2.3**). 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 **2.2.3**: 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.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure **2.2.4** 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 **2.2.4**: 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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2.3: 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 (⇌) 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:

$$mA + nB + \rightleftharpoons xC + yD \tag{2.3.1}$$

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.

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n} \tag{2.3.2}$$

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

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \tag{2.3.3}$$

is given by this expression:

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} \tag{2.3.4}$$

Example 2.3.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,O_{2(g)} \rightleftharpoons 2\,O_{3(g)}$
b. $N_{2(g)} + 3\,H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$
c. $4\,NH_{3(g)} + 7\,O_{2(g)} \rightleftharpoons 4\,NO_{2(g)} + 6\,H_2O_{(g)}$

Solution

a. $Q_c = \frac{[O_3]^2}{[O_2]^3}$
b. $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
c. $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Exercise 2.3.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
b. $C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g)$
c. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightleftharpoons 8\,CO_2(g) + 10\,H_2O(g)$

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 **2.3.1**). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

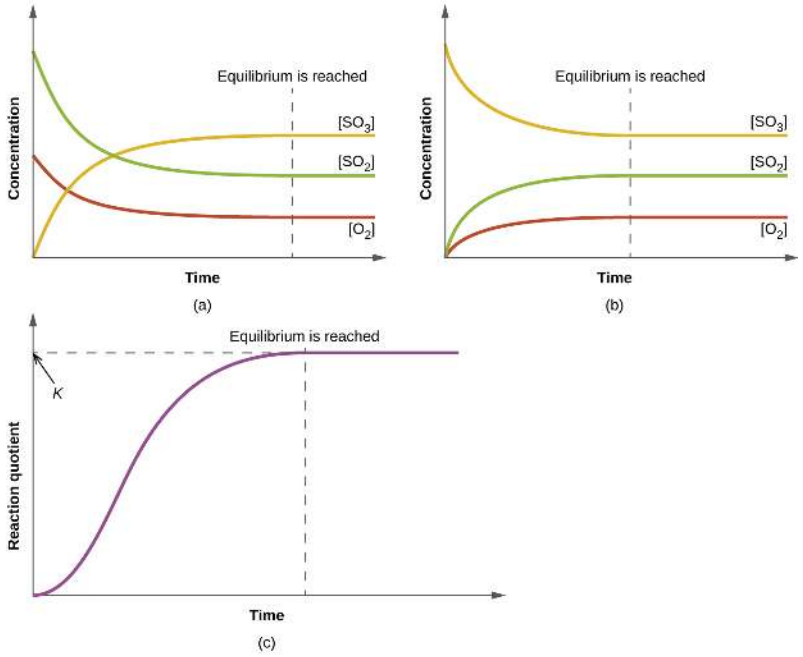


Figure **2.3.1**: (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ 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:

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y\ldots}{[A]^m[B]^n\ldots} \tag{2.3.5}$$

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 2.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

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

When 0.10 mol 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, $[NO_2] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\ M$, and [$N_2O_4$] = 0 *M*. Thus,

$$Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[N2O4]}{[NO2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

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 2.3.2

For the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

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 2.3.2 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.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 0.640 \quad T = 800°C \tag{2.3.6}$$

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 2.3.2 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.

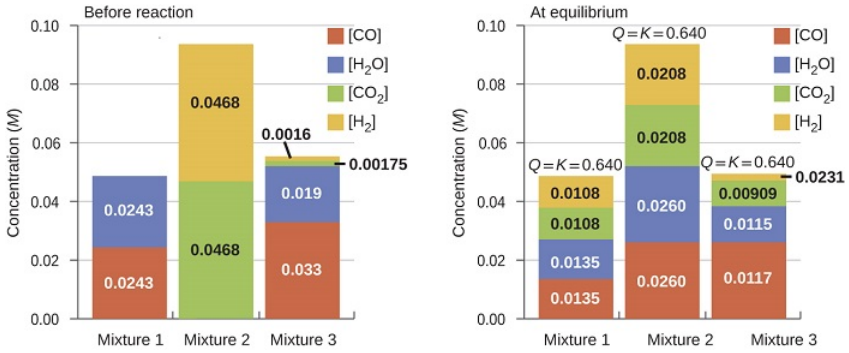


Figure 2.3.2: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 2.3.6).

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 2.3.3: 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:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[CO2][H2]}{[CO][H2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

? Exercise 2.3.3

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 **2.3.2**, 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

$$\mathrm{C_2H_2}(aq) + 2\,\mathrm{Br_2}(aq) \rightleftharpoons \mathrm{C_2H_2Br_4}(aq) \tag{2.3.7}$$

with associated equilibrium constant

$$K_c = \frac{[C2H2Br4]}{[C2H2][Br2]^2} \tag{2.3.8}$$

Example 2

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq) \tag{2.3.9}$$

with associated equilibrium constant

$$K_c = \frac{[I3-]}{[I2][I-]} \tag{2.3.10}$$

Example 3

$$\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H_3O^+}(aq) \rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + 4\,\mathrm{H_2O}(l) \tag{2.3.11}$$

with associated equilibrium constant

$$K_c = \frac{[Hg^2+]^2[HNO2]}{[Hg2^2+][NO3-][H3O+]^3} \tag{2.3.12}$$

Example 4

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \tag{2.3.13}$$

with associated equilibrium constant

$$K_c = \frac{[H3O+][F-]}{[HF]} \tag{2.3.14}$$

Example 5

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \tag{2.3.15}$$

with associated equilibrium constant

$$K_c = \frac{[NH4+][OH-]}{[NH3]} \tag{2.3.16}$$

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

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{2.3.17}$$

with associated equilibrium constant

$$K_c = \frac{[C2H4][H2]}{[C2H6]} \tag{2.3.18}$$

Example 2

$$3\,\mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{O_3}(g) \tag{2.3.19}$$

with associated equilibrium constant

$$K_c = \frac{[O3]^2}{[O2]^3} \tag{2.3.20}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{2.3.21}$$

with associated equilibrium constant

$$K_c = \frac{[NH3]^2}{[N2][H2]^3} \tag{2.3.22}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{2.3.23}$$

with associated equilibrium constant

$$K_c = \frac{[CO2]^3[H2O]^4}{[C3H8][O2]^5} \tag{2.3.24}$$

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, $\frac{n}{V}$.

$$PV = nRT \tag{2.3.25}$$

$$P = \left(\frac{n}{V}\right)RT \tag{2.3.26}$$

$$= MRT \tag{2.3.27}$$

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

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{2.3.28}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{2.3.29}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of C_2H_6; $P_{\mathrm{H_2}}$, the partial pressure of H_2; and $P_{\mathrm{C_2H_6}}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{2.3.30}$$

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:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{2.3.31}$$

with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \tag{2.3.32}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \tag{2.3.33}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \tag{2.3.34}$$

$$= K_c (RT)^{(x+y)-(m+n)} \tag{2.3.35}$$

$$= K_c (RT)^{\Delta n} \tag{2.3.36}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n} \tag{2.3.37}$$

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

$$\Delta n = (x + y) - (m + n) \tag{2.3.38}$$

Example 2.3.4: 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 2.3.4

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. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
b. $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
c. $C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g)$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\,H_2(g)$$

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

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \tag{2.3.39}$$

with associated equilibrium constant

$$K_c = [Pb^{2+}][Cl^-]^2 \tag{2.3.40}$$

Example 1

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \tag{2.3.41}$$

with associated equilibrium constant

$$K_c = \frac{1}{[CO_2]} \tag{2.3.42}$$

Example 1

$$C(s) + 2\,S(g) \rightleftharpoons CS_2(g) \tag{2.3.43}$$

with associated equilibrium constant

$$K_c = \frac{[CS2]}{[S]^2} \tag{2.3.44}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$Br_2(l) \rightleftharpoons Br_2(g) \tag{2.3.45}$$

with associated equilibrium constant

$$K_c = [\mathrm{Br_2}] \tag{2.3.46}$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using **partial pressures** instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{2.3.47}$$

with associated equilibrium constant

$$K_P = \frac{1}{P_{\mathrm{CO_2}}} \tag{2.3.48}$$

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{2.3.49}$$

with associated equilibrium constant

$$K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{2.3.50}$$

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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2.4: Shifting Equilibria - Le Châtelier'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 **2.4.1** is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 2.4.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$. *(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:

$$\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}} \qquad (2.4.1)$$

$$K_c = 50.0 \text{ at } 400°C \tag{2.4.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{2.4.3}$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g) \tag{2.4.4}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) \tag{2.4.5}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

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.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)} \tag{2.4.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + heat} \tag{2.4.7}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of $\mathrm{H_2}$ 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

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \quad \Delta H = 57.20\ \mathrm{kJ} \tag{2.4.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat + N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{2.4.9}$$

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

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.4.10}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

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

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 ($\mathrm{N_2}$) 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.

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.4.11}$$

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:

$$\mathrm{N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)} \quad \Delta H = -92.2\ \mathrm{kJ} \tag{2.4.12}$$

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 **2.4.2**).

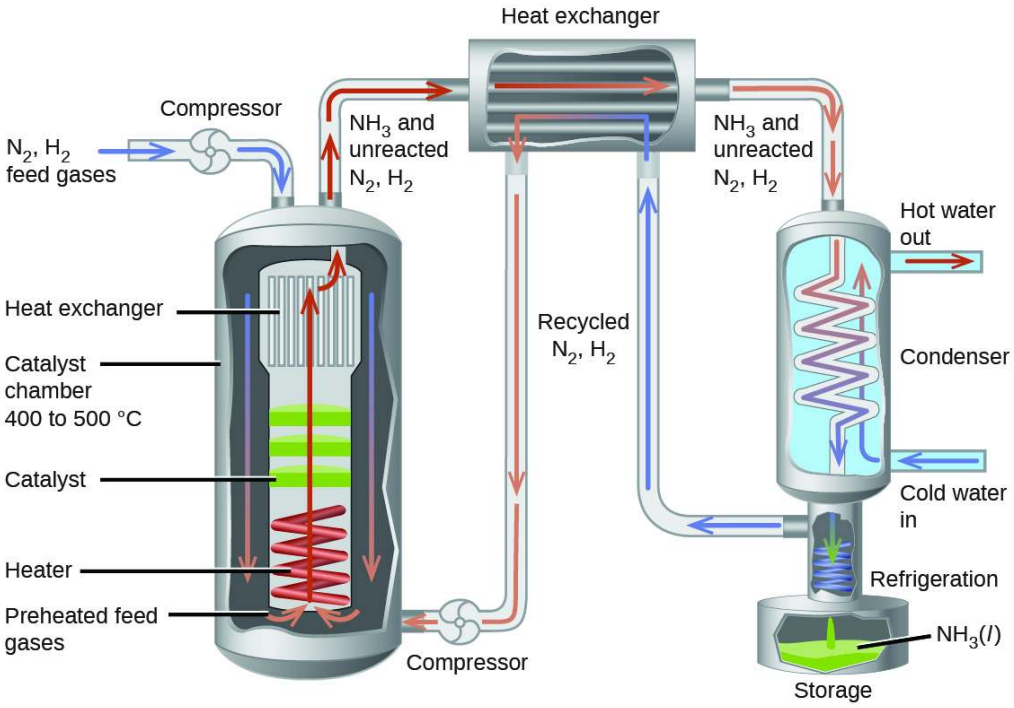


Figure **2.4.2**: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

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 **2.4.1**: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle
when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium
concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress
change to a reaction's conditions that may cause a shift in the equilibrium

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2.5: 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

$$\begin{array}{ccccc} 2\,\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\,\mathrm{H_2}(g) \\ \Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] & & \Delta[\mathrm{N_2}] = 0.11\ M & & \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \end{array} \quad \begin{array}{r} (2.5.1) \\ (2.5.2) \end{array}$$

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:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$

$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \tag{2.5.3}$$
$$-2x \qquad x \qquad 3x \tag{2.5.4}$$

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 2.5.1: Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{2.5.5}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{2.5.6}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{2.5.7}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad x \tag{2.5.8}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{2.5.9}$$
$$x \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{2.5.10}$$

Solution

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{2.5.11}$$
$$x \qquad 2x \qquad -x \tag{2.5.12}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{2.5.13}$$
$$-x \qquad -x \qquad x \tag{2.5.14}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{2.5.15}$$
$$x \qquad 5x \qquad -3x \qquad -4x \tag{2.5.16}$$

Exercise 2.5.1

Complete the changes in concentrations for each of the following reactions:

(a)

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \tag{2.5.17}$$
$$\_\_\_\_ \qquad x \qquad \_\_\_\_ \tag{2.5.18}$$

(b)

$$C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g) \tag{2.5.19}$$
$$\_\_\_\_ \qquad -2x \tag{2.5.20}$$

(c)

$$4\,NH_3(g) + 7\,H_2O(g) \rightleftharpoons 4\,NO_2(g) + 6\,H_2O(g) \tag{2.5.21}$$
$$\_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \qquad \_\_\_\_ \tag{2.5.22}$$

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 **2.5.1** 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 2.5.2: 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^- ⇌ 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 2.5.2

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 2.5.3: 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 2.5.3

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 2.5.4: 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.

$$\mathbf{PCl_5}(g) \rightleftharpoons \mathbf{PCl_3}(g) + \mathbf{Cl_2}(g) \tag{2.5.23}$$
$$-x \qquad x \qquad x \tag{2.5.24}$$

- 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 2.5.4A

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 2.5.4B

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.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \quad K_c = 6.80 \times 10^{-4}$$

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.

	$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$		
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.

	$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$		
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 2.5.5: 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 $\boldsymbol{x \ll 0.15}$, 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 2.5.5

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \quad K_c = 1.8 \times 10^{-5}$$

Assume that x is much less than 0.25 M and calculate the error in your assumption.

Answer

$\boldsymbol{[OH^-] = [NH_4^+] = 0.0021\ M}$; $[NH_3] = 0.25\ M$, 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 2.5.6: Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$\mathrm{Cu^{2+}}(aq) + 4\,\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Cu(NH_3)_4^{2+}}(aq) \quad K_c = 5.0 \times 10^{13} = \frac{[Cu(NH3)4^2+]}{[Cu^2 + (aq)][NH3]^4}$$

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

$$[\mathrm{Cu^{2+}}] = 0.010 - 0.010 = 0\ M$$

$$[\mathrm{Cu(NH_3)_4^{2+}}] = 0.010\ M$$

$$[\mathrm{NH_3}] = 1.00 - 4 \times 0.010 = 0.96\ M$$

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 2.5.6

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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2.E: Fundamental Equilibrium Concepts (Exercises)

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13.1: Chemical Equilibria Exercises

Q13.1.1

What does it mean to describe a reaction as “reversible”?

S13.1.1

The reaction can proceed in both the forward and reverse directions.

Q13.1.2

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

Q13.1.3

If a reaction is reversible, when can it be said to have reached equilibrium?

S13.1.3

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.

Q13.1.4

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

Q13.1.5

If the concentrations of products and reactants are equal, is the system at equilibrium?

S13.1.5

The concept of equilibrium does not imply equal concentrations, though it is possible.

13.2: Equilibrium Constant Exercises

Q13.2.1

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Q13.2.2

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown below:



S13.2.2

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

Q13.2.3

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

\[\ce{2NO2}(g) \rightleftharpoons \ce{N2O4}(g)\]

Q13.2.4

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

Q13.2.5

1. (a) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{AgCl}(s) \rightleftharpoons \mathbf{Ag^+}(aq) + \mathbf{Cl^-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
2. (b) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{Pb^{2+}}(aq) + \mathbf{2\,Cl^-}(aq) \rightleftharpoons \mathbf{PbCl_2}(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

S13.2.5

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \dfrac{1}{[Pb^2+][Cl-]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

Q13.2.6

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{CaCO_3}(s) \rightleftharpoons \mathbf{Ca^{2+}}(aq) + \mathbf{CO_3^-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
b. Write the expression for the equilibrium constant for the reaction represented by the equation $\mathbf{3\,Ba^{2+}}(aq) + \mathbf{2\,PO_4^{3-}}(aq) \rightleftharpoons \mathbf{Ba_3(PO_4)_2}(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

Q13.2.7

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $\mathbf{3\,C_2H_2}(g) \longrightarrow \mathbf{C_6H_6}(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

S13.2.7

Since $K_c = \dfrac{[C6H6]}{[C2H2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

Q13.2.8

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $\mathbf{KI}(aq) + \mathbf{I_2}(aq) \rightleftharpoons \mathbf{KI_3}(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

Q13.2.9

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

S13.2.9

$K_c > 1$

Q13.2.10

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

Q13.2.11

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{CH_4}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{CH_3Cl}(g) + \mathrm{HCl}(g)$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$
c. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
d. $\mathrm{BaSO_3}(s) \rightleftharpoons \mathrm{BaO}(s) + \mathrm{SO_2}(g)$
e. $\mathrm{P_4}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{P_4O_{10}}(s)$
f. $\mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{Br}(g)$
g. $\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$
h. $\mathrm{CuSO_4 \cdot 5\,H_2O}(s) \rightleftharpoons \mathrm{CuSO_4}(s) + 5\,\mathrm{H_2O}(g)$

S13.2.11

(a) $Q_c = \frac{[CH3Cl][HCl]}{[CH4][Cl2]}$; (b) $Q_c = \frac{[NO]^2}{[N2][O2]}$; (c) $Q_c = \frac{[SO3]^2}{[SO2]^2[O2]}$; (d) $Q_c = [\mathrm{SO_2}]$; (e) $Q_c = \frac{1}{[P4][O2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br2]}$; (g) $Q_c = \frac{[CO2]}{[CH4][O2]^2}$; (h) $Q_c = [\mathrm{H_2O}]^5$

Q13.2.12

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
b. $4\,\mathrm{NH_3}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 4\,\mathrm{NO}(g) + 6\,\mathrm{H_2O}(g)$
c. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$
d. $\mathrm{CO_2}(g) + \mathrm{H_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2O}(g)$
e. $\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g)$
f. $2\,\mathrm{Pb(NO_3)_2}(s) \rightleftharpoons 2\,\mathrm{PbO}(s) + 4\,\mathrm{NO_2}(g) + \mathrm{O_2}(g)$
g. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{H_2O}(l)$
h. $\mathrm{S_8}(g) \rightleftharpoons 8\,\mathrm{S}(g)$

S13.2.12

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$ $K_c = 17$; $[\mathrm{NH_3}] = 0.20\ M$, $[\mathrm{N_2}] = 1.00\ M$, $[\mathrm{H_2}] = 1.00\ M$
b. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$ $K_P = 6.8 \times 10^4$; initial pressures: $\mathrm{NH_3} = 3.0$ atm, $\mathrm{N_2} = 2.0$ atm, $\mathrm{H_2} = 1.0$ atm
c. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ $K_c = 0.230$; $[\mathrm{SO_3}] = 0.00\ M$, $[\mathrm{SO_2}] = 1.00\ M$, $[\mathrm{O_2}] = 1.00\ M$
d. $2\,\mathrm{SO_3}(g) \rightleftharpoons 2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g)$ $K_P = 16.5$; initial pressures: $\mathrm{SO_3} = 1.00$ atm, $\mathrm{SO_2} = 1.00$ atm, $\mathrm{O_2} = 1.00$ atm
e. $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g)$ $K_c = 4.6 \times 10^4$; $[\mathrm{NO}] = 1.00\ M$, $[\mathrm{Cl_2}] = 1.00\ M$, $[\mathrm{NOCl}] = 0\ M$
f. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g)$ $K_P = 0.050$; initial pressures: $\mathrm{NO} = 10.0$ atm, $\mathrm{N_2} = \mathrm{O_2} = 5$ atm

S13.2.13

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

Q13.2.14

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ $K_c = 17$; [NH_3] = 0.50 *M*, [N_2] = 0.15 *M*, [H_2] = 0.12 *M*
b. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ $K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm
c. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_c = 0.230$; [SO_3] = 2.00 *M*, [SO_2] = 2.00 *M*, [O_2] = 2.00 *M*
d. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_P = 6.5$ atm; initial pressures: SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm
e. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$ $K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm
f. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $K_c = 0.050$; [N_2] = 0.100 *M*, [O_2] = 0.200 *M*, [NO] = 1.00 *M*

Q13.2.15

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

\[\ce{N2}(g)+\ce{3H2}(g) \rightleftharpoons \ce{2NH3}(g)\]

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52

S13.2.15

The system will shift toward the reactants to reach equilibrium.

Q13.2.16

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

\(\ce{SO2Cl2}(g) \rightleftharpoons \ce{SO2}(g)+\ce{Cl2}(g)\)

[SO_2Cl_2] = 0.12 *M*, [Cl_2] = 0.16 *M* and [SO_2] = 0.050 *M*. K_c for the reaction is 0.078.

Q13.2.17

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

S13.2.17

(a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

Q13.2.18

Which of the systems described in Exercise give homogeneous equilibria? Which give heterogeneous equilibria?

Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

S13.2.19

This situation occurs in (a) and (b).

Q13.2.19

For which of the reactions in Exercise does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

Q13.2.20

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ $K_c = 0.50$ at 400°C
b. $H_2 + I_2 \rightleftharpoons 2\,HI$ $K_c = 50.2$ at 448°C
c. $Na_2SO_4 \cdot 10\,H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10\,H_2O(g)$ $K_P = 4.08 \times 10^{-25}$ at 25°C
d. $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.122$ at 50°C

S13.2.20

(a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

Q13.2.21

Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

a. $\mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \rightleftharpoons 2\,\mathrm{BrCl}(g) \quad K_c = 4.7 \times 10^{-2}$ at 25°C
b. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g) \quad K_P = 48.2$ at 500°C
c. $\mathrm{CaCl_2 \cdot 6\,H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s) + 6\,\mathrm{H_2O}(g) \quad K_P = 5.09 \times 10^{-44}$ at 25°C
d. $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad K_P = 0.196$ at 60°C

Q13.2.22

What is the value of the equilibrium constant expression for the change $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g)$ at 30 °C?

S13.2.22

$$K_P = P_{\mathrm{H_2O}} = 0.042. \tag{2.E.1}$$

Q13.2.23

Write the expression of the reaction quotient for the ionization of HOCN in water.

Q13.2.24

Write the reaction quotient expression for the ionization of NH_3 in water.

S13.2.24

$$Q_c = \frac{[NH4+][OH-]}{[HN3]} \tag{2.E.2}$$

Q13.2.25

What is the approximate value of the equilibrium constant K_P for the change $\mathrm{C_2H_5OC_2H_5}(l) \rightleftharpoons \mathrm{C_2H_5OC_2H_5}(g)$ at 25 °C. (Vapor pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

13.3: Shifting Equilbria Exercises

Q13.3.1

The following equation represents a reversible decomposition:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

S13.3.1

The amount of $CaCO_3$ must be so small that $P_{\mathrm{CO_2}}$ is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full $P_{\mathrm{CO_2}}$ required for equilibrium.

Q13.3.2

Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.

Q13.3.3

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

S13.3.3

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the

reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

Q13.3.4

What would happen to the color of the solution in part (b) of Figure if a small amount of NaOH were added and Fe(OH)3 precipitated? Explain your answer.

Q13.3.5

The following reaction occurs when a burner on a gas stove is lit:

\(\ce{CH4}(g)+\ce{2O2}(g)\rightleftharpoons\ce{CO2}(g)+\ce{2H2O}(g)\)

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

S13.3.5

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

Q13.3.6

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO3, from sulfur dioxide, SO2, and oxygen, O2, shown here. At high temperatures, the rate of formation of $SO_3$is higher, but the equilibrium amount (concentration or partial pressure) of SO3 is lower than it would be at lower temperatures.

$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \tag{2.E.3}$$

a. (a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
b. (b) Is the reaction endothermic or exothermic?

Q13.3.7a

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

\[\ce{N2}(g)+\ce{2H2}(g)\rightleftharpoons\ce{N2H4}(g) \hspace{20px} \Delta H=\ce{95\:kJ}\]

S13.3.7a

Add N_2; add H_2; decrease the container volume; heat the mixture.

Q13.3.7b

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6\,H_2(g) \rightleftharpoons 4\,PH_3(g) \quad \Delta H = 110.5\,kJ \tag{2.E.4}$$

Q13.3.8

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad \Delta H = 92\,kJ$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\,kJ$
c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g) \quad \Delta H = -285\,kJ$
d. $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad \Delta H = -176\,kJ$

S13.3.8

(a) ΔT increase = shift right, ΔP increase = shift left; (b) ΔT increase = shift right, ΔP increase = no effect; (c) ΔT increase = shift left, ΔP increase = shift left; (d) ΔT increase = shift left, ΔP increase = shift right.

Q13.3.9

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + O_2(g) \quad \Delta H = 484\ kJ$
b. $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad \Delta H = -92.2\ kJ$
c. $2\,Br(g) \rightleftharpoons Br_2(g) \quad \Delta H = -224\ kJ$
d. $H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g) \quad \Delta H = 53\ kJ$

Q13.3.10

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:

$$H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g). \tag{2.E.5}$$

Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2\,H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90.2\ kJ \tag{2.E.6}$$

b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
c. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?
d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
e. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?
f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

S13.3.10

a. $K_c = \dfrac{[CH3OH]}{[H2]^2[CO]}$;
b. [H_2] increases, [CO] decreases, [CH_3OH] increases;
c. [H_2] increases, [CO] decreases, [CH_3OH] decreases;
d. [H_2] increases, [CO] increases, [CH_3OH] increases;
e. [H_2] increases, [CO] increases, [CH_3OH] decreases;
f. no changes.

Q13.3.11

Nitrogen and oxygen react at high temperatures.

a. Write the expression for the equilibrium constant (Kc) for the reversible reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 181\ kJ \tag{2.E.7}$$

b. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?
c. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?
d. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?
e. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?
g. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

Q13.3.12

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

a. Write the expression for the equilibrium constant for the reversible reaction

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \quad \Delta H = 131.30\ \mathrm{kJ} \tag{2.E.8}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more C is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if CO is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

S13.3.12

(a) $K_c = \frac{[CO][H2]}{[H2O]}$; (b) [$H_2O$] no change, [CO] no change, [H_2] no change; (c) [H_2O] decreases, [CO] decreases, [H_2] decreases; (d) [H_2O] increases, [CO] increases, [H_2] decreases; (f) [H_2O] decreases, [CO] increases, [H_2] increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

Q13.3.13

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$\mathrm{Fe_2O_3}(s) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{Fe}(s) + 3\,\mathrm{H_2O}(g) \quad \Delta H = 98.7\ \mathrm{kJ} \tag{2.E.9}$$

b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?
e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Q13.3.14

Ammonia is a weak base that reacts with water according to this equation:

\[\ce{NH3}(aq)+\ce{H2O}(l)\rightleftharpoons\ce{NH4+}(aq)+\ce{OH-}(aq)\]

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water and why?

a. Addition of NaOH
b. Addition of HCl
c. Addition of NH_4Cl

S13.3.14

Only (b)

Q13.3.15

Acetic acid is a weak acid that reacts with water according to this equation:

\[\ce{CH3CO2H}(aq)+\ce{H2O}(aq)\rightleftharpoons\ce{H3O+}(aq)+\ce{CH3CO2-}(aq)\]

Will any of the following increase the percent of acetic acid that reacts and produces $\mathrm{CH_3CO_2^-}$ ion?

a. Addition of HCl
b. Addition of NaOH
c. Addition of $NaCH_3CO_2$

Q13.3.16

Suggest two ways in which the equilibrium concentration of Ag+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and $\mathrm{NO_3^-}$, in contact with solid AgCl.

\(\ce{Na+}(aq)+\ce{Cl-}(aq)+\ce{Ag+}(aq)+\ce{NO3-}(aq)\rightleftharpoons\ce{AgCl}(s)+\ce{Na+}(aq)+\ce{NO3-}(aq)\)

$$\Delta H = -65.9\ \mathrm{kJ}$$

S13.3.16

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

Q13.3.17

How can the pressure of water vapor be increased in the following equilibrium?

$$\ce{H2O}(l)\rightleftharpoons\ce{H2O}(g) \hspace{20px} \Delta H=\ce{41\:kJ}$$

Q13.3.18

Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

$$\ce{2Ag+}(aq)+\ce{SO4^2-}(aq)\rightleftharpoons\ce{Ag2SO4}(s)$$

Which of the following will occur?

a. Ag^+ or $\mathbf{SO_4^{2-}}$ concentrations will not change.
b. The added silver sulfate will dissolve.
c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and $\mathbf{SO_4^{2-}}$ ions combine.
d. The Ag^+ ion concentration will increase and the $\mathbf{SO_4^{2-}}$ ion concentration will decrease.

S13.3.18

(a)

Q13.3.19

The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization ($\mathbf{HX \rightleftharpoons H^+ + X^-}$)?

13.4: Equilibrium Calculations Exercises

Q13.4.1

A reaction is represented by this equation: $\mathbf{A}(aq) + 2\,\mathbf{B}(aq) \rightleftharpoons 2\,\mathbf{C}(aq) \quad K_c = 1 \times 10^3$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations ≤1 *M*, make up two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

S13.4.1

$K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

Q13.4.2

A reaction is represented by this equation: $2\,\mathbf{W}(aq) \rightleftharpoons \mathbf{X}(aq) + 2\,\mathbf{Y}(aq) \quad K_c = 5 \times 10^{-4}$

a. Write the mathematical expression for the equilibrium constant.
b. Using concentrations of ≤1 *M*, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

Q13.4.3

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$\mathbf{N_2}(g) + 3\,\mathbf{H_2}(g) \rightleftharpoons 2\,\mathbf{NH_3}(g) \qquad \mathbf{(2.E.10)}$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

S13.4.3

$K_c = 6.00 \times 10^{-2}$

Q13.4.4

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons 3\,\mathrm{H_2}(g) + \mathrm{CO}(g) \tag{2.E.11}$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

S13.4.4

$K_c = 0.50$

Q13.4.5

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 3.3×10^{-3}% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2\,\mathrm{NO_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \tag{2.E.12}$$

Q13.4.6

Calculate the value of the equilibrium constant K_P for the reaction $2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

S13.4.6

The equilibrium equation is $K_P = 1.9 \times 10^3$

Q13.4.7

When heated, iodine vapor dissociates according to this equation:

$$\mathrm{I_2}(g) \rightleftharpoons 2\,\mathrm{I}(g) \tag{2.E.13}$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

Q13.4.8

A sample of ammonium chloride was heated in a closed container.

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g) \tag{2.E.14}$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

S13.4.8

$K_P = 3.06$

Q13.4.9

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the transformation at 60 °C?

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \tag{2.E.15}$$

Q13.4.10

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad (2.E.16)$$
$$\_\_\_\_ \quad \_\_\_\_ \quad +x \quad (2.E.17)$$
$$\_\_\_\_ \quad \_\_\_\_ \quad 0.125\ M \quad (2.E.18)$$

(b)

$$4\,NH_3(g) + 3\,O_2(g) \rightleftharpoons 2\,N_2(g) + 6\,H_2O(g) \quad (2.E.19)$$
$$\_\_\_\_ \quad 3x \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.20)$$
$$\_\_\_\_ \quad 0.24\ M \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.21)$$

(c) Change in pressure:

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g) \quad (2.E.22)$$
$$\_\_\_\_ \quad x \quad \_\_\_\_ \quad (2.E.23)$$
$$\_\_\_\_ \quad 25\ \text{torr} \quad \_\_\_\_ \quad (2.E.24)$$

(d) Change in pressure:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g) \quad (2.E.25)$$
$$\_\_\_\_ \quad x \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.26)$$
$$\_\_\_\_ \quad 5\ \text{atm} \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.27)$$

(e)

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \quad (2.E.28)$$
$$x \quad \_\_\_\_ \quad (2.E.29)$$
$$1.03 \times 10^{-4}\ M \quad \_\_\_\_ \quad (2.E.30)$$

(f) change in pressure:

$$Ni(s) + 4\,CO(g) \rightleftharpoons Ni(CO)_4(g) \quad (2.E.31)$$
$$4x \quad \_\_\_\_ \quad (2.E.32)$$
$$0.40\ \text{atm} \quad \_\_\_\_ \quad (2.E.33)$$

S13.4.10

a. $-2x$, $2x$, $-0.250\ M$, $0.250\ M$;
b. $4x$, $-2x$, $-6x$, $0.32\ M$, $-0.16\ M$, $-0.48\ M$;
c. $-2x$, $3x$, -50 torr, 75 torr;
d. x, $-x$, $-3x$, 5 atm, -5 atm, -15 atm;
e. x, $1.03 \times 10^{-4}\ M$; (f) x, 0.1 atm.

Q13.4.11

Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g) \quad (2.E.34)$$
$$\_\_\_\_ \quad \_\_\_\_ \quad +2x \quad (2.E.35)$$
$$\_\_\_\_ \quad \_\_\_\_ \quad 1.50\ M \quad (2.E.36)$$

(b)

$$CS_2(g) + 4\,H_2(g) \rightleftharpoons CH_4(g) + 2\,H_2S(g) \quad (2.E.37)$$
$$x \quad \_\_\_\_ \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.38)$$
$$0.020\ M \quad \_\_\_\_ \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.39)$$

(c) Change in pressure:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g) \quad (2.E.40)$$
$$x \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.41)$$
$$1.50\ \text{atm} \quad \_\_\_\_ \quad \_\_\_\_ \quad (2.E.42)$$

(d) Change in pressure:

$$2\,NH_3(g) + 2\,O_2(g) \rightleftharpoons N_2O(g) + 3\,H_2O(g) \quad (2.E.43)$$
$$\_\_\_\_ \quad \_\_\_\_ \quad \_\_\_\_ \quad x \quad (2.E.44)$$
$$\_\_\_\_ \quad \_\_\_\_ \quad \_\_\_\_ \quad 60.6\ \text{torr} \quad (2.E.45)$$

(e)

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \quad (2.E.46)$$
$$x \quad \_\_\_\_ \quad (2.E.47)$$
$$9.8 \times 10^{-6}\ M \quad \_\_\_\_ \quad (2.E.48)$$

(f) Change in pressure:

$$Fe(s) + 5\,CO(g) \rightleftharpoons Fe(CO)_4(g) \quad (2.E.49)$$
$$\_\_\_\_ \quad x \quad (2.E.50)$$
$$\_\_\_\_ \quad 0.012\ \text{atm} \quad (2.E.51)$$

Q13.4.12

Why are there no changes specified for Ni in Exercise, part (f)? What property of Ni does change?

S13.4.12

Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

Q13.4.13

Why are there no changes specified for NH_4HS in Exercise, part (e)? What property of NH_4HS does change?

Q13.4.14

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.50 \text{ at } 400\ ^\circ\text{C} \quad (2.E.52)$$

Calculate the equilibrium molar concentration of NH_3.

S13.4.14

$[NH_3] = 9.1 \times 10^{-2}\ M$

Q13.4.16

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448\ ^\circ\text{C}$$

Q13.4.17

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_P = 4.7 \times 10^{-2} \quad (2.E.53)$$

S13.4.17

$P_{BrCl} = 4.9 \times 10^{-2}$ atm

Q13.4.18

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad K_P = 1.6 \text{ at } 990\ ^\circ\text{C} \quad (2.E.54)$$

Q13.4.12

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \quad K_c = 4.90 \times 10^2 \text{ at } 550\ ^\circ\text{C}$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

S13.4.12

$[CO] = 2.0 \times 10^{-4}\ M$

Q13.4.13

Carbon reacts with water vapor at elevated temperatures.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad K_c = 0.2 \text{ at } 1000\ ^\circ C$$

What is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500\ M$ at 1000 °C?

Q13.4.14

Sodium sulfate 10−hydrate, $Na_2SO_4 \cdot 10H_2O$, dehydrates according to the equation

$$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \tag{2.E.55}$$

with $K_p = 4.08 \times 10^{-25}$ at 25°C. What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4 \cdot 10H_2O$ and $NaSO_4$?

S13.4.14

$P_{H_2O} = 3.64 \times 10^{-3}$ atm

Q13.4.15

Calcium chloride 6−hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

$$CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \quad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$?

Q13.4.16

A student solved the following problem and found the equilibrium concentrations to be $[SO_2] = 0.590\ M$, $[O_2] = 0.0450\ M$, and $[SO_3] = 0.260\ M$. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3] = 0.500\ M$, $[SO_2] = 0\ M$, and $[O_2] = 0.350\ M$?

S13.4.16

Calculate Q based on the calculated concentrations and see if it is equal to K_c. Because Q does equal 4.32, the system must be at equilibrium.

Q13.4.16

A student solved the following problem and found $[N_2O_4] = 0.16\ M$ at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 M?

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = 160 \tag{2.E.56}$$

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 1.07 \times 10^{-5} \text{ in chloroform}$$

(b) Show that the change is small enough to be neglected.

S13.4.16

(a)

- $[NO_2] = 1.17 \times 10^{-3}\ M$
- $[N_2O_4] = 0.128\ M$

(b) Percent error $= \frac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.

Q13.4.17

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

a. Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

$$\mathrm{COCl_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{Cl_2}(g) \quad K_c = 2.2 \times 10^{-10} \tag{2.E.57}$$

b. Show that the change is small enough to be neglected.

Q13.4.18

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$$2\,\mathrm{H_2S}(g) \rightleftharpoons 2\,\mathrm{H_2}(g) + \mathrm{S_2}(g) \quad K_P = 2.2 \times 10^{-6}$$

(b) Show that the change is small enough to be neglected.

S13.4.18

(a)

- $[H_2S] = 0.810$ atm
- $[H_2] = 0.014$ atm
- $S_2] = 0.0072$ atm

(b) The $2x$ is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring $2x$ is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the "5% test." The error is, indeed, negligible.

Q13.4.19

What are all concentrations after a mixture that contains $[H_2O] = 1.00\ M$ and $[Cl_2O] = 1.00\ M$ comes to equilibrium at 25 °C?

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g) \quad K_c = 0.0900 \tag{2.E.58}$$

Q13.4.20

What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5] = 2.00\ M$?

$$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \quad K_c = 0.0211 \tag{2.E.59}$$

S13.4.20

$[PCl_3] = 1.80\ M$; $[PC_3] = 0.195\ M$; $[PCl_3] = 0.195\ M$.

Q13.4.21

Calculate the pressures of all species at equilibrium in a mixture of NOCl, NO, and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:

$$2\,\mathrm{NOCl}(g) \rightleftharpoons 2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \quad K_P = 4.0 \times 10^{-4} \tag{2.E.60}$$

Q13.4.22

Calculate the equilibrium concentrations of NO, O_2, and NO_2 in a mixture at 250 °C that results from the reaction of 0.20 *M* NO and 0.10 *M* O_2. (Hint: *K* is large; assume the reaction goes to completion then comes back to equilibrium.)

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = 2.3 \times 10^5 \text{ at } 250\ ^\circ C \tag{2.E.61}$$

S13.4.22

- $[NO_2]$ = 0.19 *M*
- [NO] = 0.0070 *M*
- $[O_2]$ = 0.0035 *M*

Q13.4.23

Calculate the equilibrium concentrations that result when 0.25 *M* O_2 and 1.0 *M* HCl react and come to equilibrium.

$$4\,HCl(g) + O_2(g) \rightleftharpoons 2\,Cl_2(g) + 2\,H_2O(g) \quad K_c = 3.1 \times 10^{13} \tag{2.E.62}$$

Q13.4.24

One of the important reactions in the formation of smog is represented by the equation

$$O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g) \quad K_P = 6.0 \times 10^{34} \tag{2.E.63}$$

What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of 1.2×10^{-8} atm and NO with a pressure of 1.2×10^{-8} atm comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion then comes back to equilibrium.)

S13.4.24

$P_{O_3} = 4.9 \times 10^{-26}$ atm

Q13.4.24

Calculate the pressures of NO, Cl_2, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl_2. (Hint: K_P is small; assume the reverse reaction goes to completion then comes back to equilibrium.)

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_P = 2.5 \times 10^3$$

Q13.4.25

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2\,HI \quad K_c = 50.2 \text{ at } 448\ ^\circ C$$

S13.4.25

507 g

Q13.4.26

Butane exists as two isomers, *n*−butane and isobutane.


Three Lewis structures are shown. The first is labeled, “n dash Butane,” and has a C H subscript 3 single bonded to a C H subscript 2 group. This C H subscript 2 group is single bonded to another C H subscript 2 group which is single bonded to a C H subscript 3 group. The second is labeled, “iso dash Butane,” and is composed of a C H group single bonded to three C H subscript 3 groups. The third structure shows a chain of atoms: “C H subscript 3, C H subscript 2, C H subscript 2, C H subscript 3,” a double-headed arrow, then a carbon atom single bonded to three C H subscript 3 groups as well as a hydrogen atom.

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

Q13.4.27

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of $CaCO_3$ at that temperature?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

S13.4.27

330 g

Q13.4.28

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$\mathrm{H_2}(g) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g) + \mathrm{CO}(g) \tag{2.E.64}$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

Q13.4.29

At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{\mathrm{N_2O_4}} = 0.70\ \mathrm{atm}$ and $P_{\mathrm{NO_2}} = 0.30\ \mathrm{atm}$.

a. Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
b. Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C.

S13.4.29

(a) Both gases must increase in pressure.

(b) $P_{\mathrm{N_2O_4}} = 8.0\ \mathrm{atm}$ and $P_{\mathrm{NO_2}} = 1.0\ \mathrm{atm}$

Q13.4.30

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{2.E.65}$$

a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

Q13.4.31

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

\[\ce{CO}(g)+\ce{H2O}(g) <=> \ce{CO2}(g)+\ce{H2}(g)\)]

a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?
b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

S13.4.31

(a) 0.33 mol.

(b) $[CO]^2 = 0.50\ M$ Added H_2 forms some water to compensate for the removal of water vapor and as a result of a shift to the left after H_2 is added.

Q13.4.32a

Antimony pentachloride decomposes according to this equation:

$$\mathrm{SbCl_5}(g) \rightleftharpoons \mathrm{SbCl_3}(g) + \mathrm{Cl_2}(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

Q13.4.32b

Consider the reaction between H_2 and O_2 at 1000 K

$$\ce{2H2}(g)+\ce{O2}(g)⇌\ce{2H2O}(g) \hspace{20px} K_P=\dfrac{(P_{\ce{H2O}})^2}{(P_{\ce{O2}})(P_{\ce{H2}})^3}=1.33×10^{20}$$

If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components?

S13.4.32b

$P_{H_2} = 8.64 \times 10^{-11}$ atm

$P_{\ce{O2}}=0.250\:\ce{atm}$

$P_{\ce{H2O}}=0.500\:\ce{atm}$

Q13.4.33

An equilibrium is established according to the following equation

$$\begin{aligned} &\mathrm{Hg_2^{2+}}(aq) + \mathrm{NO_3^-}(aq) + 3\,\mathrm{H^+}(aq) \\ &\rightleftharpoons 2\,\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \quad K_c = 4.6 \end{aligned} \tag{2.E.66}$$

What will happen in a solution that is 0.20 *M* each in Hg_2^{2+}, NO_3^-, H^+, Hg^{2+}, and HNO_2?

a. Hg_2^{2+} will be oxidized and NO_3^- reduced.
b. Hg_2^{2+} will be reduced and NO_3^- oxidized.
c. Hg^{2+} will be oxidized and HNO_2 reduced.
d. Hg^{2+} will be reduced and HNO_2 oxidized.
e. There will be no change because all reactants and products have an activity of 1.

Q13.4.34

Consider the equilibrium

$$4\,\mathrm{NO_2}(g) + 6\,\mathrm{H_2O}(g) \rightleftharpoons 4\,\mathrm{NH_3}(g) + 7\,\mathrm{O_2}(g) \tag{2.E.67}$$

a. What is the expression for the equilibrium constant (K_c) of the reaction?
b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
c. If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2?
d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

S13.4.34

(a) $K_c = \dfrac{[NH3]^4[O2]^7}{[NO2]^4[H2O]^6}$. (b) [$NH_3$] must increase for Q_c to reach K_c. (c) That decrease in pressure would decrease [NO_2]. (d) $P_{O_2} = 49$ torr

Q13.4.35

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$\mathrm{HbO_2}(aq) + \mathrm{H_3O^+}(aq) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2{-}Hb{-}H^+} + \mathrm{O_2}(g) + \mathrm{H_2O}(l)$$

1. (a) Write the equilibrium constant expression for this reaction.

2. (b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

Q13.4.36

The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.

$$\mathrm{C_{12}H_{22}O_{11}}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(aq) + \mathrm{C_6H_{12}O_6}(aq)$$

Rate = $k[C_{12}H_{22}O_{11}]$

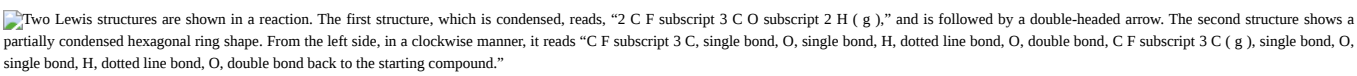
In neutral solution, $k = 2.1 \times 10^{-11}$/s at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $C_6H_{12}O_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27 °C. What are the concentrations of glucose, fructose, and sucrose after a 0.150 *M* aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1.

S13.4.36

[fructose] = 0.15 *M*

Q13.4.37

The density of trifluoroacetic acid vapor was determined at 118.1 °C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid.



Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of $K_P = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

S13.4.37

$$P_{\mathrm{N_2O_3}} = 1.90 \text{ atm and } P_{\mathrm{NO}} = P_{\mathrm{NO_2}} = 1.90 \text{ atm}$$

Q13.4.38

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*?

Q13.4.39

A 0.010 *M* solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25 °C. A 0.010 *M* solution of the weak acid HB has an osmotic pressure of 0.345 atm under the same conditions.

(a) Which acid has the larger equilibrium constant for ionization

$$\text{HA } [\mathrm{HA}(aq) \rightleftharpoons \mathrm{A^-}(aq) + \mathrm{H^+}(aq)] \text{ or HB } [\mathrm{HB}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{B^-}(aq)]?$$

(b) What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.)

S13.4.39

(a) HB ionizes to a greater degree and has the larger K_c.

(b) $K_c(HA) = 5 \times 10^{-4}$

$K_c(\text{HB}) = 3 \times 10^{-3}$

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CHAPTER OVERVIEW

3: Acid-Base Equilibria

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General Chemistry

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

3.1: Brønsted-Lowry Acids and Bases
3.2: pH and pOH
3.3: Relative Strengths of Acids and Bases
3.4: Hydrolysis of Salt Solutions
3.5: Polyprotic Acids
3.6: Buffers
3.7: Acid-Base Titrations
3.E: Acid-Base Equilibria (Exercises)

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3.1: Brønsted-Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

Later, 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:

$$H^+ + OH^- \rightarrow H_2O \tag{3.1.1}$$

We call the product that remains after an acid donates a proton the conjugate base of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{3.1.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{3.1.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{3.1.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{3.1.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{3.1.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{3.1.7}$$

We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{3.1.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{3.1.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{3.1.10}$$

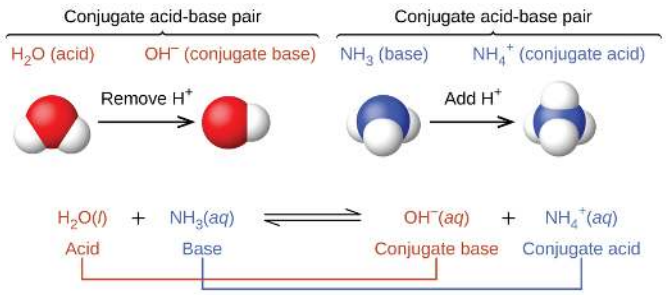
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{3.1.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{3.1.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{3.1.13}$$

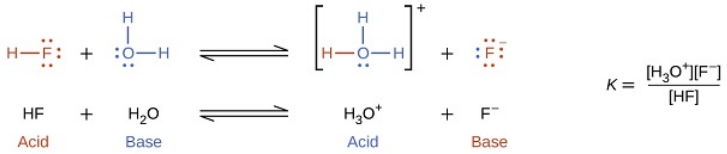
$$F^- + H^+ \rightleftharpoons HF \tag{3.1.14}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



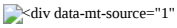
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

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:

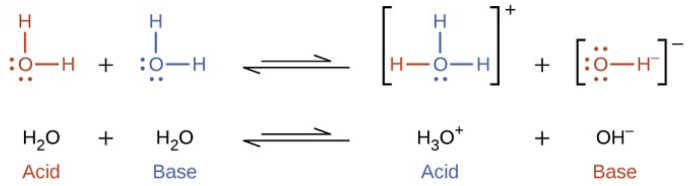


This figure has two rows. In both rows, a chemical reaction is shown. In the first, structural formulas are provided. In this model, in purple, an H atom is connected to an F atom with a single bond. The F atom has pairs of electron dots at the top, right, and bottom. This is followed by a plus sign, which is followed in green by an O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. A double arrow follows. To the right, in brackets is a structure with a central O atom in green, with green H atoms singly bonded above and to the right. A pair of green electron dots is on the lower side of the O atom. To the left of the green O atom, a purple H atom is singly bonded. This is followed by a plus sign and an F atom in purple with pairs of electron dots above, right, below, and to the left. This atom also has a superscript negative sign. The reaction is written in symbolic form below. H F is labeled in purple below as “Acid subscript 1.” This is followed by plus H subscript 2 O, which is labeled in green below as “Base subscript 2.” A double sided arrow follows. To the right is H subscript 3 O superscript plus, which is labeled in green as below in as “Acid subscript 2.” This is followed by plus and F surrounded by 4 pairs of dots and superscript negative. The label below in purple reads, “Base subscript 1.” To the right of the reactions is the formula, K subscript a equals left bracket H subscript 3 O superscript plus right bracket left bracket F superscript negative right bracket all over left bracket H F right bracket.

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:



This figure has two rows. In both rows, a chemical reaction is shown. In the first, structural formulas are provided. In this model, in purple, O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. This is followed by a plus sign, which is followed in green by an O atom which has H atoms singly bonded above and to the right. The O atom has pairs of electron dots on its left and lower sides. A double arrow follows. To the right, in brackets is a structure with a central O atom in green, with green H atoms singly bonded above and to the right. A pair of green electron dots is on the lower side of the O atom. To the left of the green O atom, a purple H atom is singly bonded. Outside the brackets to the right is a superscript plus. This is followed by a plus sign and an O atom in purple with pairs of electron dots above, left, and below. An H atom is singly bonded to the right. This atom has a superscript negative sign. The reaction is written in symbolic form below. H subscript 2 O is labeled in purple below as “Acid subscript 1.” This is followed by plus H subscript 2 O, which is labeled in green below as “Base subscript 2.” A double sided arrow follows. To the right is H subscript 3 O superscript plus, which is labeled in green as below in as “Acid subscript 2.” This is followed by plus and O with pairs of dots above, below, and to the left with a singly bonded H on the right with a superscript negative. The label below in purple reads, “ Base subscript 1.”

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \quad K_w = [H_3O^+][OH^-] \tag{3.1.15}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and

hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 50-times larger than the value at 25 °C.

Example 3.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14}$$

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 3.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.12 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 3.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$ A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-]$$
$$= (2.0 \times 10^{-6})(5.0 \times 10^{-9})$$
$$= 1.0 \times 10^{-14}$$

? Exercise 3.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

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:

$$HCO^-{}_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}{}_{3(aq)} + H_3O^+{}_{(aq)} \quad (3.1.16)$$

$$HCO^-{}_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-{}_{(aq)} \quad (3.1.17)$$

✓ Example 3.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

a. as an acid with OH^-
b. as a base with HI

Solution

a. $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3{}^{2-}(aq) + H_2O_{(l)}$
b. $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

? Exercise 3.1.3

Write separate equations representing the reaction of $H_2PO_4^-$

a. as a base with HBr
b. as an acid with OH^-

Answer a

$$H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$$

Answer b

$$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4{}^{2-}(aq) + H_2O_{(l)}$$

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, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

Key Equations

- $$K_w = [H_3O^+][OH^-\,] = 1.0 \times 10^{-14} \text{ (at 25 °C)}$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

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3.2: pH and pOH

Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{3.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{3.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{3.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{3.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{3.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{3.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{3.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{3.2.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{3.2.9}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{3.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{3.2.11}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

When $pH = 7$ Solutions are not Neutral

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

$$\begin{aligned} pOH &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table **3.2.1**).

Table **3.2.1**: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure **3.2.1** shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

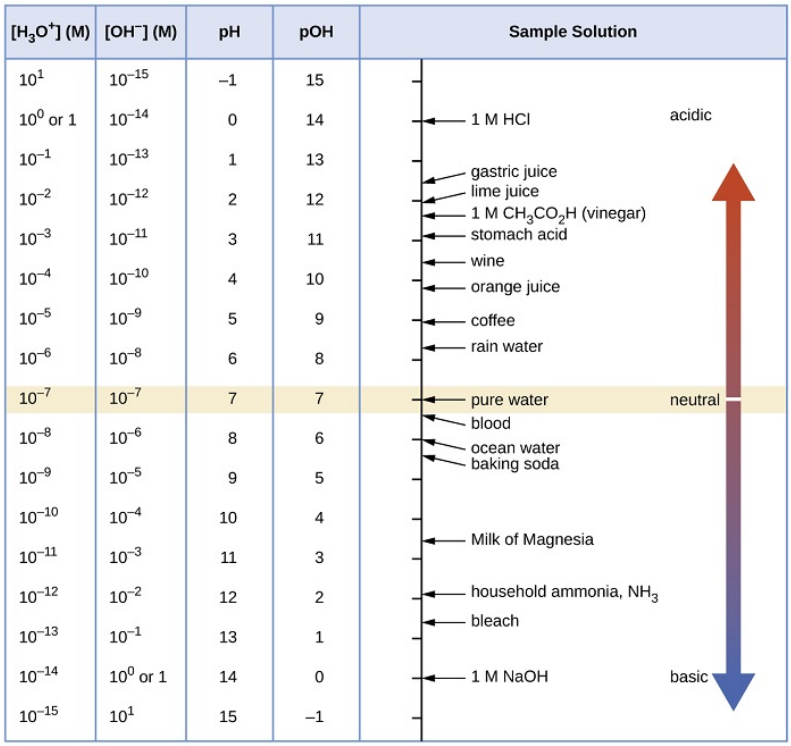


Figure **3.2.1**: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

A table is provided with 5 columns. The first column is labeled “left bracket H subscript 3 O superscript plus right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript 1, including 10 superscript 0 or 1, 10 superscript negative 1, decreasing by single powers of 10 to 10 superscript negative 15. The second column is labeled “left bracket O H superscript negative right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript negative 15, increasing by single powers of 10 to including 10 superscript 0 or 1, and 10 superscript 1. The third column is labeled “p H.” Values listed in this column are integers beginning at negative 1, increasing by ones up to 14. The fourth column is labeled “p O H.” Values in this column are integers beginning at 15, decreasing by ones up to negative 1. The fifth column is labeled “Sample Solution.” A vertical line at the left of the column has tick marks corresponding to each p H level in the table. Substances are listed next to this line segment with line segments connecting them to the line to show approximate p H and p O H values. 1 M H C l is listed at a p H of 0. Gastric juices are listed at a p H of about 1.5. Lime juice is listed at a p H of about 2, followed by 1 M C H subscript 3 C O subscript 2 H, followed by stomach acid at a p H value of nearly 3. Wine is listed around 3.5. Coffee is listed just past 5. Pure water is listed at a p H of 7. Pure blood is just beyond 7. Milk of Magnesia is listed just past a p H of 10.5. Household ammonia is listed just before a pH of 12. 1 M N a O H is listed at a p H of 0. To the right of this labeled arrow is an arrow that points up and down through the height of the column. A beige strip passes through the table and to this double headed arrow at p H 7. To the left of the double headed arrow in this beige strip is the label “neutral.” A narrow beige strip runs through the arrow. Just above and below this region, the arrow is purple. It gradually turns to a bright red as it extends upward. At the top of the arrow, near the head of the arrow is the label “acidic.” Similarly, the lower region changes color from purple to blue moving to the bottom of the column. The head at this end of the arrow is labeled “basic.”

Example 3.2.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 3.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 3.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3$$

$$\log[\mathrm{H_3O^+}] = -7.3$$

$$[\mathrm{H_3O^+}] = 10^{-7.3}$$

or

$$[\mathrm{H_3O^+}] = \text{antilog of} - 7.3$$

$$[\mathrm{H_3O^+}] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the "inverse" log, of −7.3, or calculate $10^{-7.3}$.)

Exercise 3.2.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{3.2.12}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)} \tag{3.2.13}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{3.2.14}$$

$$\mathrm{H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4^-\,(aq)} \tag{3.2.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are

formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure **3.2.2**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



Figure **3.2.2**: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

✔ Example **3.2.3**: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125$ M:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10$$

? Exercise **3.2.3**

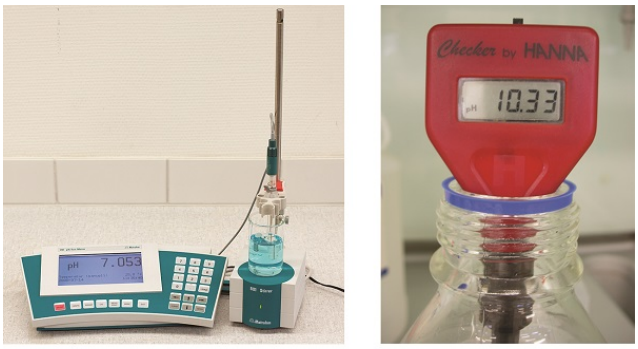
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure **3.2.3**).



(a) (b)

Figure **3.2.3**: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

This figure contains two images. The first, image a, is of an analytical digital p H meter on a laboratory counter. The second, image b, is of a portable hand held digital p H meter.

The pH of a solution may also be visually estimated using colored indicators (Figure **3.2.3**).



(a) (b)

Figure **3.2.4**: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

This figure contains two images. The first shows a variety of colors of solutions in labeled beakers. A red solution in a beaker is labeled “0.10 M H C l.” An orange solution is labeled “0.10 M C H subscript 3 C O O H.” A yellow-orange solution is labeled “0.1 M N H subscript 4 C l.” A yellow solution is labeled “deionized water.” A second solution beaker is labeled “0.10 M K C l.” A green solution is labeled “0.10 M aniline.” A blue solution is labeled “0.10 M N H subscript 4 C l (a q).” A final beaker containing a dark blue solution is labeled “0.10 M N a O H.” Image b shows pHydrion paper that is used for measuring pH in the range of p H from 1 to 12. The color scale for identifying p H based on color is shown along with several of the test strips used to evaluate p H.

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; $\mathbf{pH = -\log H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathbf{pOH = -\log[OH^-]}$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathbf{pH = -\log[H_3O^+]}$
- $\mathbf{pOH = -\log[OH^-]}$
- $[H_3O^+] = 10^{-\text{pH}}$
- $[OH^-] = 10^{-\text{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

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3.3: Relative Strengths of Acids and Bases

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 3.3.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 3.3.1: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

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:

$$\%\ \text{ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{3.3.1}$$

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 3.3.1: Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[H3O+]_{eq}}{[HNO2]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq).$$

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 3.3.1) 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 3.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

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 3.3.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, **B**:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

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, $\mathrm{HA} - \mathrm{A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

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 **3.3.2**).

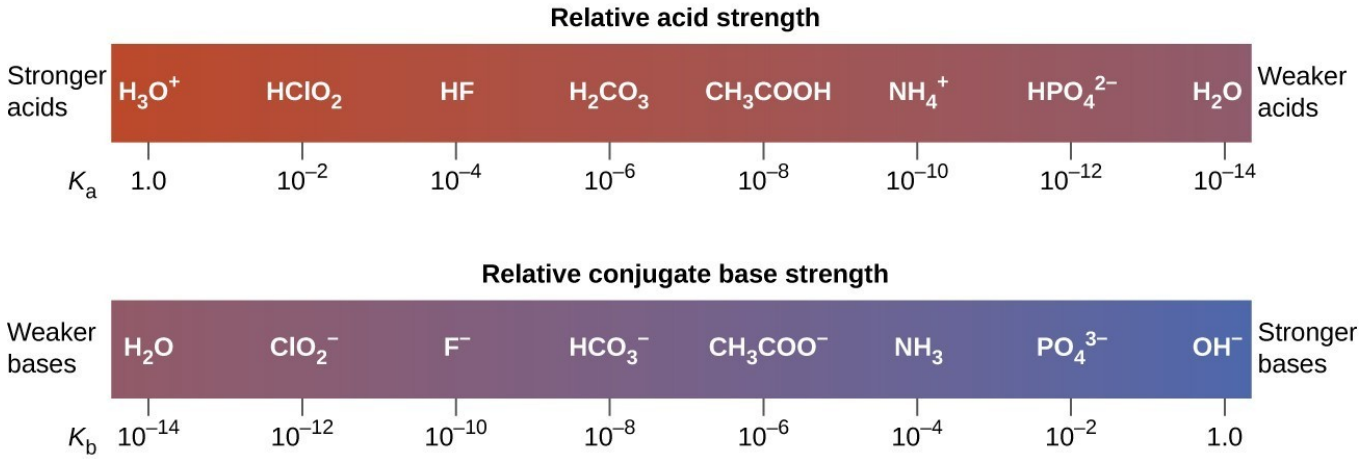


Figure **3.3.2**: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure **3.3.3** lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure **3.3.3** are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure **3.3.3** form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure **3.3.3** exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

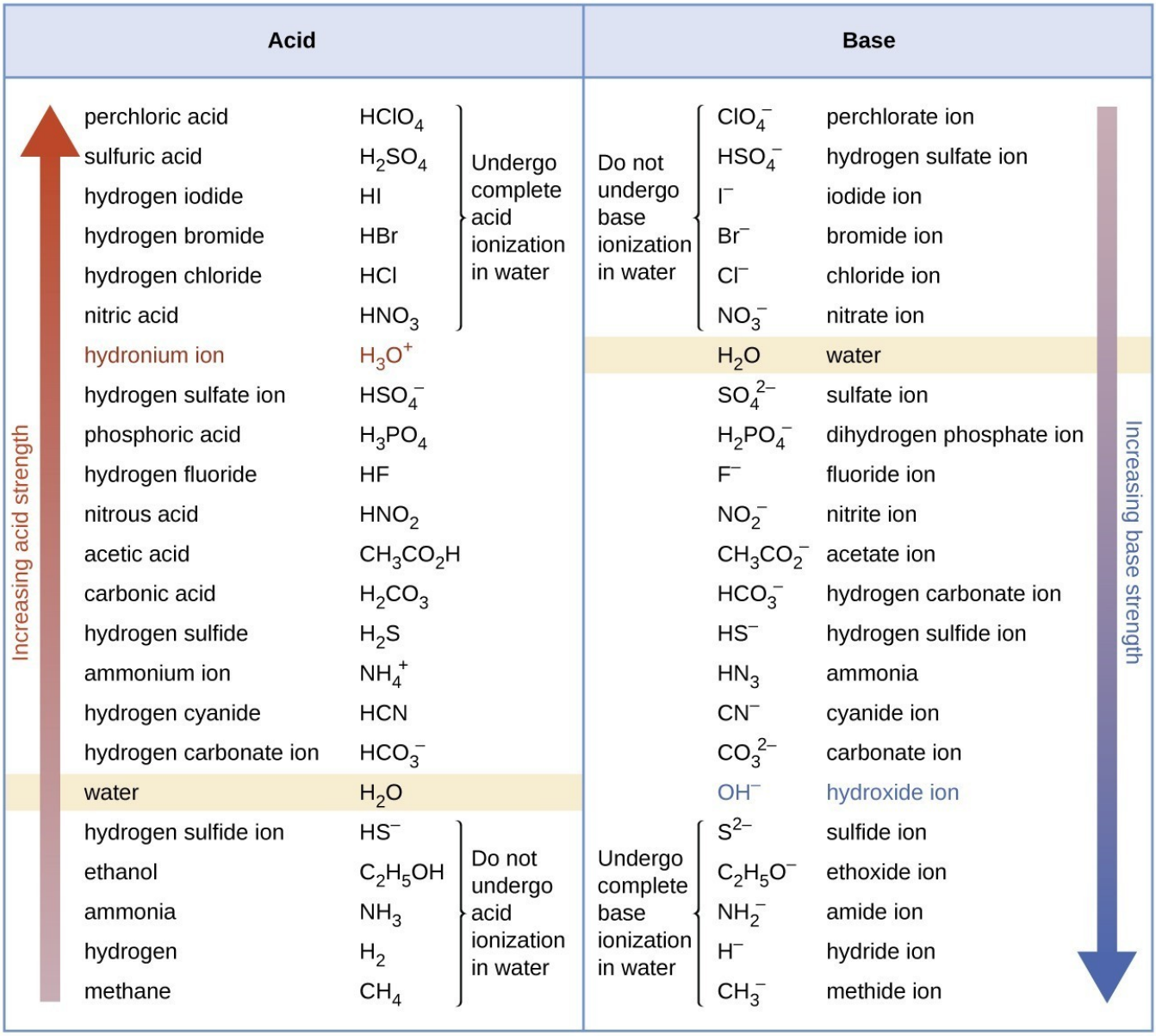


Figure **3.3.3**: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure **3.3.3**. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

✔ Example **3.3.2**: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 3.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 4.9×10^{-10}. The ionization constant of NH_4^+ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$).

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 3.3.4). 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 **3.3.4**: 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 **3.3.1**: 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 **3.3.1** 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 **3.3.5**: 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 **3.3.2** and Table E2.

Table **3.3.2**: 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 3.3.3: 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 3.3.3

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 3.3.4: 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 3.3.4

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 3.3.5: Determination of K_a or K_b from pH

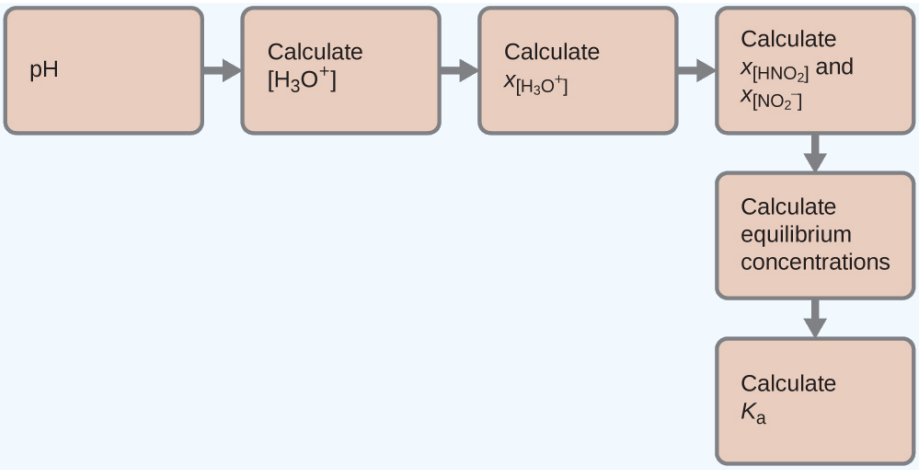
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

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 3.3.5

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 3.3.6: 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 3.3.6: 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%

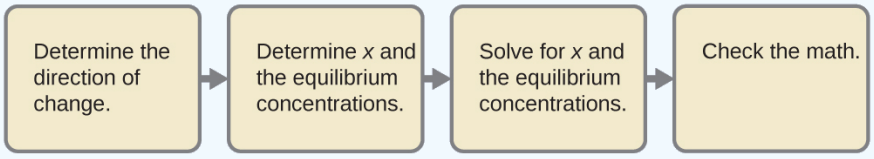
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 3.3.7: 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 3.3.6. 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 3.3.7

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.

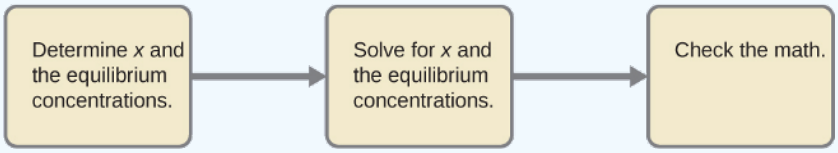
Example 3.3.8: Equilibrium Concentrations in a Solution of a Weak Acid

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 3.3.8

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 [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 $\mathbf{CH_4 < NH_3 < H_2O < HF}$; across the third row, it is $\mathbf{SiH_4 < PH_3 < H_2S < HCl}$ (see Figure **3.3.6**).

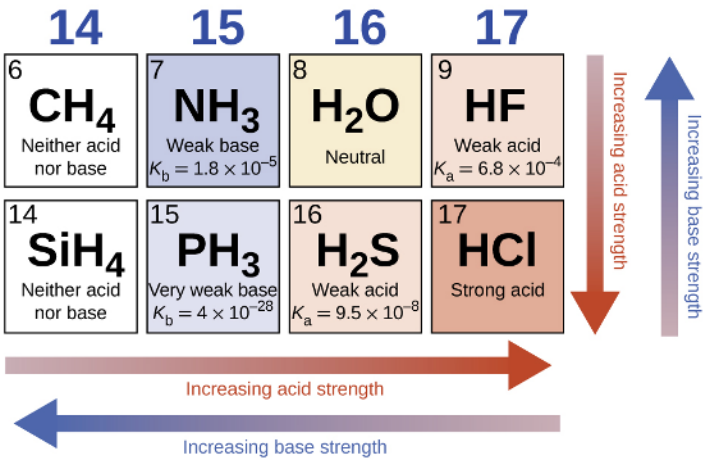
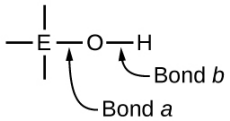


Figure **3.3.6**: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

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, $\mathbf{O_2S(OH)_2}$, sulfurous acid, $\mathbf{OS(OH)_2}$, nitric acid, $\mathbf{O_2NOH}$, perchloric acid, $\mathbf{O_3ClOH}$, aluminum hydroxide, $\mathbf{Al(OH)_3}$, calcium hydroxide, $\mathbf{Ca(OH)_2}$, and potassium hydroxide, $\mathbf{KOH}$:



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 **3.3.7**).

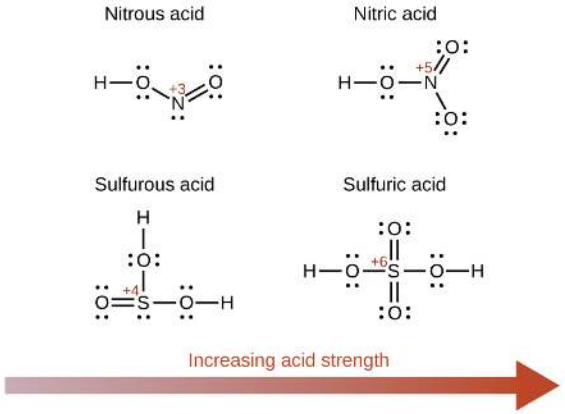


Figure **3.3.7**: As the oxidation number of the central atom E increases, the acidity also increases.

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:

$$\mathbf{[Al(H_2O)_3(OH)_3](aq) + OH^-(aq) \rightleftharpoons H_2O(\mathit{l}) + [Al(H_2O)_2(OH)_4]^-(aq)}$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $\mathbf{Al(H_2O)_3(OH)_3}$ 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:

$$\mathbf{3\,H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3\,H_2O(\mathit{l})}$$

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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3.4: Hydrolysis of Salt Solutions

Learning Objectives

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the process that causes solutions of certain metal ions to be acidic

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as HCl(aq) and NaOH(aq) will react to form a neutral solution since the conjugate partners produced are of negligible strength:

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

2. A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base.
3. A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
4. A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated K values of the conjugates must be compared.

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 M HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure **3.4.1**). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.

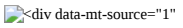


Figure **3.4.1**: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

Salts of Weak Bases and Strong Acids

When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a weak acid. For example, ammonium chloride, NH_4Cl, is a salt formed by the reaction of the weak base ammonia with the strong acid HCl:

$$\mathrm{NH_3}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NH_4Cl}(aq)$$

A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since HCl is a strong acid. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:

$$\mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq)$$

The equilibrium equation for this reaction is simply the ionization constant. K_a, for the acid $\mathrm{NH_4^+}$:

$$\frac{[H3O+][NH3]}{[NH4+]} = K_a$$

We will not find a value of K_a for the ammonium ion in Table E1. However, it is not difficult to determine K_a for $\mathrm{NH_4^+}$ from the value of the ionization constant of water, K_w, and K_b, the ionization constant of its conjugate base, NH_3, using the following relationship:

$$K_w = K_a \times K_b$$

This relation holds for any base and its conjugate acid or for any acid and its conjugate base.

Example 3.4.1: pH of a Solution of a Salt of a Weak Base and a Strong Acid

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride, $[C_6H_5NH_3^+]Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of aniline hydrochloride?

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$$

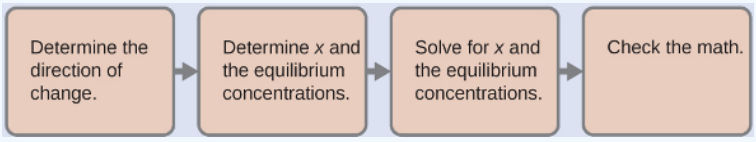
Solution

The new step in this example is to determine K_a for the $C_6H_5NH_3^+$ ion. The $C_6H_5NH_3^+$ ion is the conjugate acid of a weak base. The value of K_a for this acid is not listed in Table E1, but we can determine it from the value of K_b for aniline, $C_6H_5NH_2$, which is given as 4.6×10^{-10} :

$$K_a(\text{for } C_6H_5NH_3^+) \times K_b(\text{for } C_6H_5NH_2) = K_w = 1.0 \times 10^{-14}$$

$$K_a(\text{for } C_6H_5NH_3^+) = \frac{K_w}{K_b(\text{for } C_6H_5NH_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Now we have the ionization constant and the initial concentration of the weak acid, the information necessary to determine the equilibrium concentration of H_3O^+, and the pH:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

With these steps we find $[H_3O^+] = 2.3 \times 10^{-3}$ *M* and pH = 2.64

Exercise 3.4.1

a. Do the calculations and show that the hydronium ion concentration for a 0.233-*M* solution of $C_6H_5NH_3^+$ is 2.3×10^{-3} and the pH is 2.64.

b. What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions NH_4^+ and NO_3^-. Use the data in Table E1 to determine K_b for the ammonium ion. Which is the stronger acid $C_6H_5NH_3^+$ or NH_4^+?

Answer a

$K_a(\text{for } NH_4^+) = 5.6 \times 10^{-10}$, $[H_3O^+]$ = 7.5 × 10−6 M

Answer b

$C_6H_5NH_3^+$ is the stronger acid (a) (b) .

Salts of Weak Acids and Strong Bases

When we neutralize a weak acid with a strong base, we get a salt that contains the conjugate base of the weak acid. This conjugate base is usually a weak base. For example, sodium acetate, $NaCH_3CO_2$, is a salt formed by the reaction of the weak acid acetic acid with the strong base sodium hydroxide:

$$CH_3CO_2H(aq) + NaOH(aq) \longrightarrow NaCH_3CO_2(aq) + H_2O(aq)$$

A solution of this salt contains sodium ions and acetate ions. The sodium ion has no effect on the acidity of the solution. However, the acetate ion, the conjugate base of acetic acid, reacts with water and increases the concentration of hydroxide ion:

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

The equilibrium equation for this reaction is the ionization constant, K_b, for the base $CH_3CO_2^-$. The value of K_b can be calculated from the value of the ionization constant of water, K_w, and K_a, the ionization constant of the conjugate acid of the anion using the equation:

$$_w = K_a \times K_b$$

For the acetate ion and its conjugate acid we have:

$$K_b(\text{for } CH_3CO_2^-) = \frac{K_w}{K_a(\text{for } CH_3CO_2H)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Some handbooks do not report values of K_b. They only report ionization constants for acids. If we want to determine a K_b value using one of these handbooks, we must look up the value of K_a for the conjugate acid and convert it to a K_b value.

Example 3.4.2: Equilibrium of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[CH_3CO_2^-] = 0.050\ M$ and $[OH^-] = 2.5 \times 10^{-6}\ M$ at equilibrium. The reaction is:

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

Solution

We are given two of three equilibrium concentrations and asked to find the missing concentration. If we can find the equilibrium constant for the reaction, the process is straightforward.

The acetate ion behaves as a base in this reaction; hydroxide ions are a product. We determine K_b as follows:

$$K_b(\text{for } CH_3CO_2^-) = \frac{K_w}{K_a(\text{for } CH_3CO_2H)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now find the missing concentration:

$$K_b = \frac{[CH3CO2H][OH-]}{[CH3CO2-]} = 5.6 \times 10^{-10}$$

$$= \frac{[CH_3CO_2H](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving this equation we get $[CH_3CO_2H] = 1.1 \times 10^{-5}\ M$.

Exercise 3.4.2

What is the pH of a 0.083-M solution of CN^-? Use 4.9×10^{-10} as K_a for HCN. Hint: We will probably need to convert pOH to pH or find $[H_3O^+]$ using $[OH^-]$ in the final stages of this problem.

Answer

11.16

Equilibrium in a Solution of a Salt of a Weak Acid and a Weak Base

In a solution of a salt formed by the reaction of a weak acid and a weak base, to predict the pH, we must know both the K_a of the weak acid and the K_b of the weak base. If $K_a > K_b$, the solution is acidic, and if $K_b > K_a$, the solution is basic.

Example 3.4.3: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. KBr
b. $NaHCO_3$

c. NH_4Cl
d. Na_2HPO_4
e. NH_4F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

a. The K^+ cation and the Br^- anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.
b. The Na^+ cation is a spectator, and will not affect the pH of the solution; the $\mathbf{HCO_3^-}$ anion is amphiprotic.The K_a of $\mathbf{HCO_3^-}$ is 4.7×10^{-11}, so the K_b of its conjugate base is $\frac{\mathbf{1.0 \times 10^{-14}}}{\mathbf{4.7 \times 10^{-11}}} = \mathbf{2.1 \times 10^{-4}}$. Since $K_b >> K_a$, the solution is basic.
c. The $\mathbf{NH_4^+}$ ion is acidic and the Cl^- ion is a spectator. The solution will be acidic.
d. The Na^+ ion is a spectator and will not affect the pH of the solution, while the $\mathbf{HPO_4^{2-}}$ ion is amphiprotic. The K_a of $\mathbf{HPO_4^{2-}}$ is 4.2×10^{-13} and its K_b is $\frac{\mathbf{1.0 \times 10^{-14}}}{\mathbf{4.2 \times 10^{-13}}} = \mathbf{2.4 \times 10^{-2}}$. Because $K_b >> K_a$, the solution is basic.
e. The $\mathbf{NH_4^+}$ ion is listed as being acidic, and the F^- ion is listed as a base, so we must directly compare the K_a and the K_b of the two ions. K_a of $\mathbf{NH_4^+}$ is 5.6×10^{-10}, which seems very small, yet the K_b of F^- is 1.4×10^{-11}, so the solution is acidic, since $K_a > K_b$.

? Exercise 3.4.3

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. K_2CO_3
b. $CaCl_2$
c. KH_2PO_4
d. $(NH_4)_2CO_3$
e. $AlBr_3$

Answer a

basic

Answer b

neutral

Answer c

acidic

Answer d

basic

Answer e

acidic

The Ionization of Hydrated Metal Ions

If we measure the pH of the solutions of a variety of metal ions we will find that these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion, $\mathbf{Al(H_2O)_6^{3+}}$, dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this $\mathbf{Al(H_2O)_6^{3+}}$ cluster as well:

$$\mathbf{Al(NO_3)_3}(s) + \mathbf{6\,H_2O}(l) \longrightarrow \mathbf{Al(H_2O)_6^{3+}}(aq) + \mathbf{3\,NO_3^-}(aq)$$

We frequently see the formula of this ion simply as "$Al^{3+}(aq)$", without explicitly noting the six water molecules that are the closest ones to the aluminum ion and just describing the ion as being solvated in water (hydrated). This is similar to the simplification of the formula of the hydronium ion, H_3O^+ to H^+. However, in this case, the hydrated aluminum ion is a weak acid (Figure **3.4.2**) and donates a proton to a water molecule. Thus, the hydration becomes important and we may use formulas that show the extent of hydration:

$$Al(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq) \quad K_a = 1.4 \times 10^{-5}$$

As with other polyprotic acids, the hydrated aluminum ion ionizes in stages, as shown by:

$$Al(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq)$$

$$Al(H_2O)_5(OH)^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_4(OH)_2{}^+(aq)$$

$$Al(H_2O)_4(OH)_2{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq)$$

Note that some of these aluminum species are exhibiting amphiprotic behavior, since they are acting as acids when they appear on the left side of the equilibrium expressions and as bases when they appear on the right side.

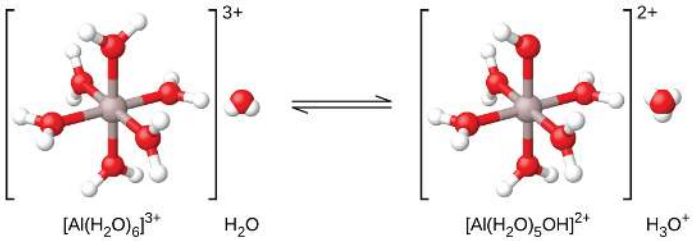


Figure **3.4.2**: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

A reaction is shown using ball and stick models. On the left, inside brackets with a superscript of 3 plus outside to the right is structure labeled "[A l (H subscript 2 O) subscript 6] superscript 3 plus." Inside the brackets is s central grey atom to which 6 red atoms are bonded in an arrangement that distributes them evenly about the central grey atom. Each red atom has two smaller white atoms attached in a forked or bent arrangement. Outside the brackets to the right is a space-filling model that includes a red central sphere with two smaller white spheres attached in a bent arrangement. Beneath this structure is the label "H subscript 2 O." A double sided arrow follows. Another set of brackets follows to the right of the arrows which have a superscript of two plus outside to the right. The structure inside the brackets is similar to that on the left, except a white atom is removed from the structure. The label below is also changed to "[A l (H subscript 2 O) subscript 5 O H] superscript 2 plus." To the right of this structure and outside the brackets is a space filling model with a central red sphere to which 3 smaller white spheres are attached. This structure is labeled "H subscript 3 O superscript plus."

However, the ionization of a cation carrying more than one charge is usually not extensive beyond the first stage. Additional examples of the first stage in the ionization of hydrated metal ions are:

$$Fe(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Fe(H_2O)_5(OH)^{2+}(aq) \quad K_a = 2.74$$

$$Cu(H_2O)_6{}^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cu(H_2O)_5(OH)^+(aq) \quad K_a = 6.3$$

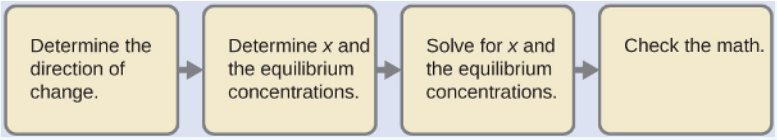
$$Zn(H_2O)_4{}^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^+(aq) \quad K_a = 9.6$$

✔ Example 3.4.4: Hydrolysis of $[Al(H_2O)_6]^{3+}$

Calculate the pH of a 0.10-*M* solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion $[Al(H_2O)_6]^{3+}$ in solution.

Solution

In spite of the unusual appearance of the acid, this is a typical acid ionization problem.



A reaction is shown using ball and stick models. On the left, inside brackets with a superscript of 3 plus outside to the right is structure labeled “[A l (H subscript 2 O) subscript 6] superscript 3 plus.” Inside the brackets is s central grey atom to which 6 red atoms are bonded in an arrangement that distributes them evenly about the central grey atom. Each red atom has two smaller white atoms attached in a forked or bent arrangement. Outside the brackets to the right is a space-filling model that includes a red central sphere with two smaller white spheres attached in a bent arrangement. Beneath this structure is the label “H subscript 2 O.” A double sided arrow follows. Another set of brackets follows to the right of the arrows which have a superscript of two plus outside to the right. The structure inside the brackets is similar to that on the left, except a white atom is removed from the structure. The label below is also changed to “[A l (H subscript 2 O) subscript 5 O H] superscript 2 plus.” To the right of this structure and outside the brackets is a space filling model with a central red sphere to which 3 smaller white spheres are attached. This structure is labeled “H subscript 3 O superscript plus.”

1. *Determine the direction of change*. The equation for the reaction and K_a are:

$$\mathrm{Al(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_5(OH)^{2+}}(aq) \quad K_a = 1.4 \times 10^{-5}$$

The reaction shifts to the right to reach equilibrium.

2. *Determine x and equilibrium concentrations.* Use the table

:

	$\mathrm{Al(H_2O)_6^{3+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{Al(H_2O)_5(OH)^{2+}}$		
Initial concentration (*M*)	0.10	~0	0
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	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 in the first column: Initial concentration (M), Change (M), Equilibrium concentration (M). The second column has the header of “A l (H subscript 2 O) subscript 6 superscript 3 positive sign plus H subscript 2 O equilibrium arrow H subscript 3 O superscript positive sign plus A l (H subscript 2 O) subscript 5 (O H) superscript 2 positive sign.” Under the second column is a subgroup of four columns and three rows. The first column has the following: 0.10 (which appears in red), negative x, 0.10 minus x. The second column is blank. The third column has the following: approximately 0, x, x. The fourth column has the following: 0, x, x.

Solve for x and the equilibrium concentrations. Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

1.

$$K_a = \frac{[H3O+][Al(H2O)5(OH)^2+]}{[Al(H2O)6^3+]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Solving this equation gives:

$$x = 1.2 \times 10^{-3}\ M$$

From this we find:

$$[\mathrm{H_3O^+}] = 0 + x = 1.2 \times 10^{-3}\ M$$

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 2.92 (\text{an acidic solution})$$

Check the work. The arithmetic checks; when 1.2×10^{-3} *M* is substituted for *x*, the result = K_a.

Exercise 3.4.4

What is $[Al(H_2O)_5(OH)^{2+}]$ in a 0.15-*M* solution of $Al(NO_3)_3$ that contains enough of the strong acid HNO_3 to bring $[H_3O^+]$ to 0.10 *M*?

Answer

$2.1 \times 10^{-5}\ M$

The constants for the different stages of ionization are not known for many metal ions, so we cannot calculate the extent of their ionization. However, practically all hydrated metal ions other than those of the alkali metals ionize to give acidic solutions. Ionization increases as the charge of the metal ion increases or as the size of the metal ion decreases.

Summary

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic. Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative K_a and K_b of the ions involved.

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3.5: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

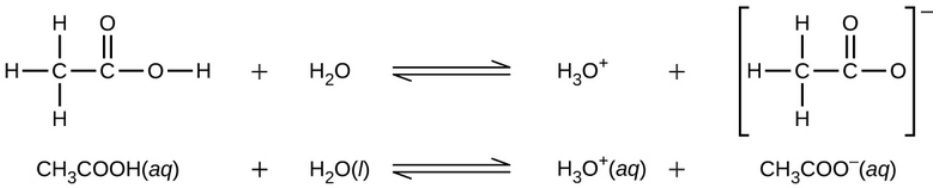
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as $\mathbf{HCl}$, $\mathbf{HNO_3}$, and $\mathbf{HCN}$ that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathbf{HCl}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{Cl^-}(aq)$$

$$\mathbf{HNO_3}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{NO_3^-}(aq)$$

$$\mathbf{HCN}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{CN^-}(aq)$$

Even though it contains four hydrogen atoms, acetic acid, $\mathbf{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($\mathbf{-COOH}$) reacts with bases:



This image contains two equilibrium reactions. The first shows a C atom bonded to three H atoms and another C atom. The second C atom is double bonded to an O atom and also forms a single bond to another O atom. The second O atom is bonded to an H atom. There is a plus sign and then the molecular formula H subscript 2 O. An equilibrium arrow follows the H subscript 2 O. To the right of the arrow is H subscript 3 O superscript positive sign. There is a plus sign. The final structure shows a C atom bonded the three H atoms and another C atom. This second C atom is double bonded to an O atom and single bonded to another O atom. The entire structure is in brackets and a superscript negative sign appears outside the brackets. The second reaction shows C H subscript 3 C O O H (a q) plus H subscript 2 O (l) equilibrium arrow H subscript 3 O (a q) plus C H subscript 3 C O O superscript negative sign (a q).

Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathbf{H_2SO_4}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HSO_4^-}(aq)$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$\mathbf{HSO_4^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{SO_4^{2-}}(aq)$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathbf{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathbf{H_2CO_3}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{HCO_3^-}(aq)$$

with

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the HCO_3^- formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and HCO_3^- are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 3.5.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\ M$?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7} \qquad \text{(equilibrium step 1)}$$

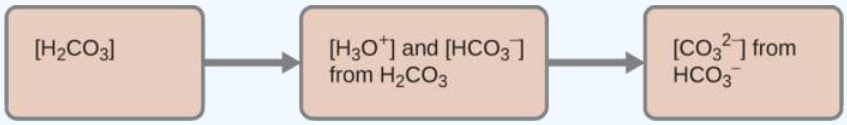
$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \quad K_{a2} = 4.7 \times 10^{-11} \qquad \text{(equilibrium step 2)}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than HCO_3^-, so H_2CO_3 is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and HCO_3^- produced by ionization of H_2CO_3.
2. Then we determine the concentration of CO_3^{2-} in a solution with the concentration of H_3O^+ and HCO_3^- determined in (1).

To summarize:



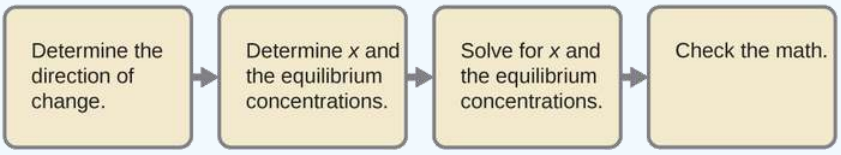
Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “left bracket H subscript 2 C O subscript 3 right bracket.” The second is labeled “left bracket H subscript 3 O superscript plus right bracket and left bracket H C O subscript 3 superscript negative right bracket from H subscript 2 C O subscript 3.” The third is labeled “left bracket C O subscript 3 superscript 2 negative right bracket from H C O subscript 3 superscript negative.”

1. First Ionization: Determine the concentrations of H_3O^+ *and* HCO_3^-.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



Four tan rectangles are shown that are connected with right pointing arrows. The first is labeled “Determine the direction of change.” The second is labeled “Determine x and the equilibrium concentrations.” The third is labeled “Solve for x and the equilibrium concentrations.” The fourth is labeled “Check the math.”

An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$H_2CO_3(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$HCO_3^-(aq)$
Initial (M)	$0.033\ M$	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H3O+][HCO3-]}{[H2CO3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H3O+][CO3^2-]}{[HCO3-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[CO_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[H_2CO_3] = 0.033\ M$, $[H_3O^+] = 1.2 \times 10^{-4}$, and $[HCO_3^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$.

? Exercise 3.5.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1M$, $[H_3O^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3^-}(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH^-}(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid
: acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base
: base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid
: acid containing one ionizable hydrogen atom per molecule

stepwise ionization
: process in which an acid is ionized by losing protons sequentially

triprotic acid
: acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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3.6: Buffers

Learning Objectives

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure **3.6.1**). A solution of acetic acid ($\mathbf{CH_3COOH}$ and sodium acetate $\mathbf{CH_3COONa}$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($\mathbf{NH_3\,(aq)}$) and ammonium chloride ($\mathbf{NH_4Cl\,(aq)}$).



Figure **3.6.1**: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \longrightarrow \mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$\mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq) \longrightarrow \mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure **3.6.2**).

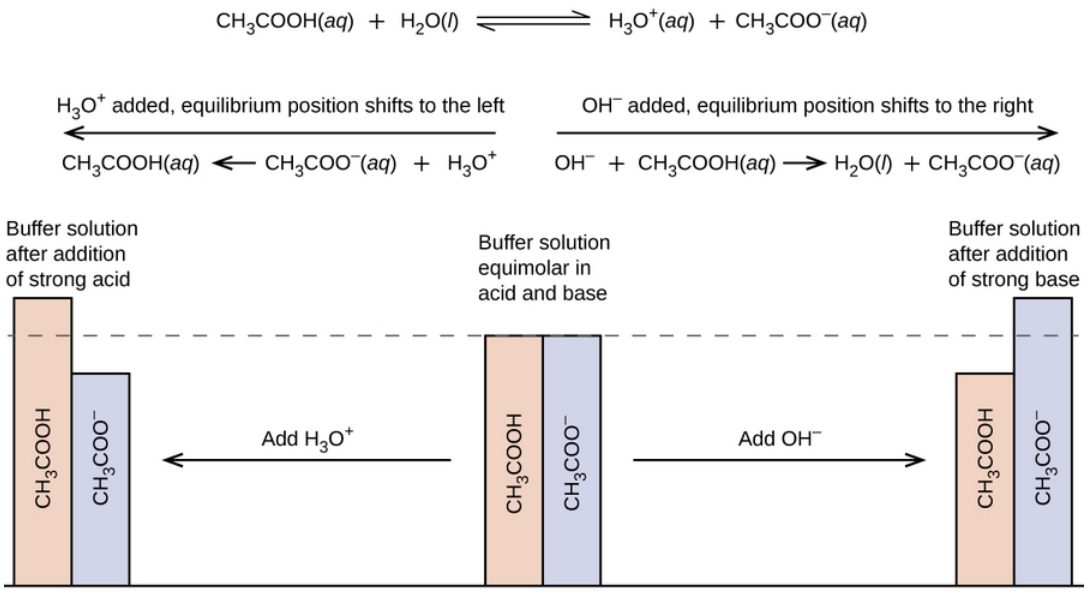


Figure **3.6.2**: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example 3.6.1: pH Changes in Buffered and Unbuffered Solutions

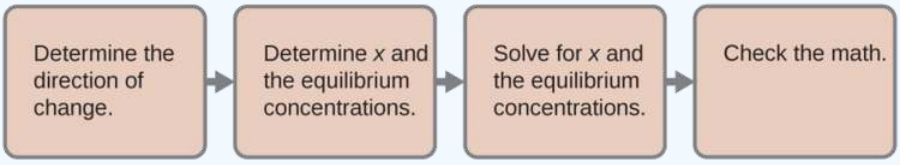
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

Solution

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



1. *Determine the direction of change.* The equilibrium in a mixture of H_3O^+, $\mathrm{CH_3CO_2^-}$, and CH_3CO_2H is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

The equilibrium constant for CH_3CO_2H is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form H_3O^+.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

	$[CH_3CO_2H] + [H_2O] \rightleftharpoons H_3O^+ + [CH_3CO_2^-]$		
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	$0.10 + x$

- *Solve for x and the equilibrium concentrations.* We find:

$$x = 1.8 \times 10^{-5}\ M$$

- and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

Thus:

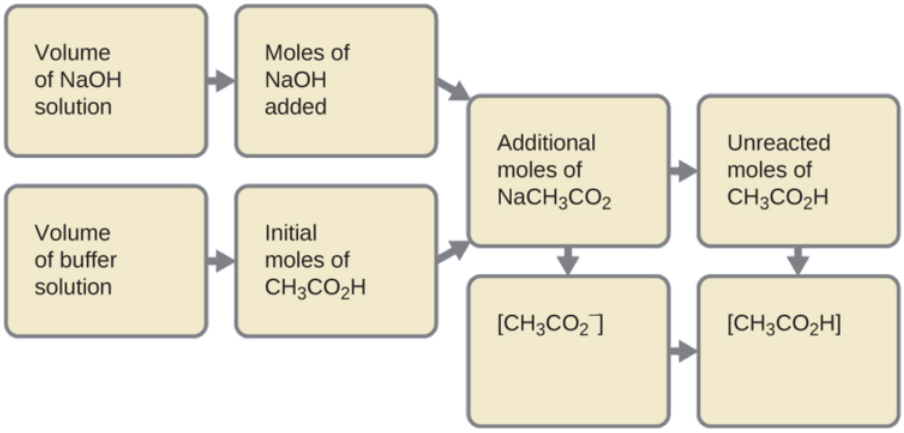
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. *Determine the moles of NaOH*. One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010\,\cancel{L} \times \left(\frac{0.10\ \text{mol NaOH}}{1\,\cancel{L}}\right) = 1.0 \times 10^{-4}\ \text{mol NaOH}$$

2. *Determine the moles of CH_2CO_2H*. Before reaction, 0.100 L of the buffer solution contains:

$$0.100\,\cancel{L} \times \left(\frac{0.100\ \text{mol } CH_3CO_2H}{1\,\cancel{L}}\right) = 1.00 \times 10^{-2}\ \text{mol } CH_3CO_2H$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

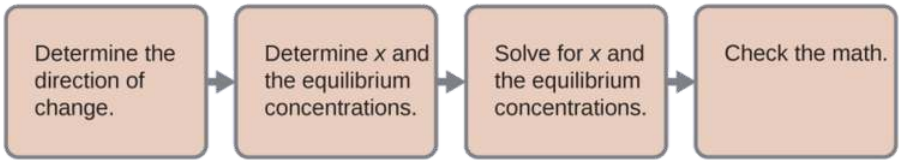
$$[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]$$

4. *Find the molarity of the products.* After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098\ M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100\ M$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in CH_3CO_2H and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a 1.8×10^{-5}-*M* solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-5}-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100 \text{ L} \times \left(\frac{1.8 \times 10^{-5} \text{ mol HCl}}{1 \text{ L}} \right) = 1.8 \times 10^{-6} \text{ mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M \text{ NaOH}}{0.101 \text{ L}} = 9.7 \times 10^{-4}\ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[OH^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

? Exercise 3.6.1

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8×10^{-5} *M* HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = 1.0×10^{-4} moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure **3.6.3**). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



Figure **3.6.3**: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure **3.6.4** shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

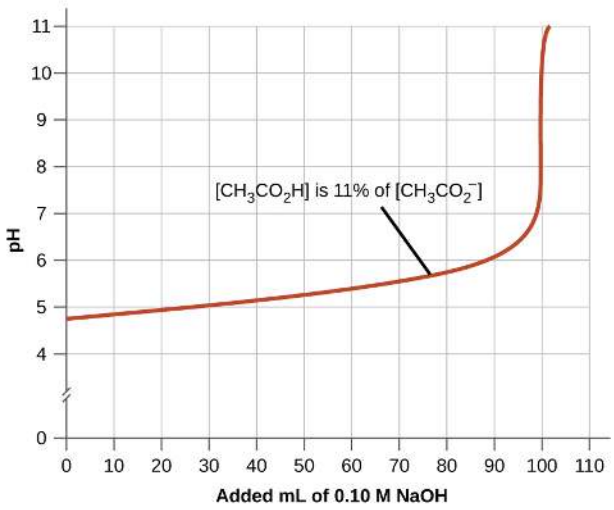


Figure **3.6.4**: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch approximation, to calculate the pH of buffer solutions. It is important to note that the "x is small" assumption must be valid to use this equation.

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathbf{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathbf{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathbf{HCO_3^-}$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Key Equations

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$

Glossary

buffer capacity

amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solutions

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3.7: Acid-Base Titrations

Learning Objectives

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

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

Titration Curves

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

Example 3.7.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH the titration curve is shown in Figure **3.7.1**. Calculate the pH at these volumes of added base solution:

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

Solution

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

The total initial amount of the hydronium ions is:

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

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

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

The total volume becomes:

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

The number of moles of H_3O^+ becomes:

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

The concentration of H_3O^+ is:

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

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

with the definition of $\mathbf{pH}$:

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) \tag{3.7.1}$$

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

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

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

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

In this case:

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

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

then using the definition of $\boldsymbol{pOH}$ and its relationship to $\boldsymbol{pH}$ in room temperature aqueous solutios (Equation 3.7.1):

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

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

(a) X = 0 mL

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

then using the definition of $\boldsymbol{pH}$ (Equation 3.7.1):

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

(b) X = 12.50 mL

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

then using the definition of $\boldsymbol{pH}$ (Equation 3.7.1):

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

(c) X = 25.00 mL

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

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

and

$$pH = 7.000$$

as described earlier.

(d) X = 37.50 mL

In this case:

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

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

then using the definition of pH (Equation 3.7.1):

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

Exercise 3.7.1

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

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

Answer a

0.00: 1.000

Answer b

15.0: 1.5111

Answer c

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

Answer d

40.0: 12.523

In Example **3.7.1**, we calculated pH at four points during a titration. Table **3.7.1** shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

Table **3.7.1**: pH Values in the Titrations of a Strong Acid with a Strong Base and of a Weak Acid with a Strong Base

Volume of 0.100 M NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 M HCl[1]	pH Values 0.100 M CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

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

The simplest acid-base reactions are those of a strong acid with a strong base. Table **3.7.1** shows data for the titration of a 25.0-mL sample of 0.100 *M* hydrochloric acid with 0.100 *M* sodium hydroxide. The values of the pH measured after successive additions of small amounts of NaOH are listed in the first column of this table, and are graphed in Figure **3.7.1**, in a form that is called a titration curve. The pH increases slowly at first, increases rapidly in the middle portion of the curve, and then increases slowly again. The point of inflection (located at the midpoint of the vertical part of the curve) is the equivalence point for the titration. It indicates when equivalent quantities of acid and base are present. For the titration of a strong acid with a strong base, the equivalence point occurs at a pH of 7.00 and the points on the titration curve can be calculated using solution stoichiometry (Table **3.7.1** and Figure **3.7.1**).

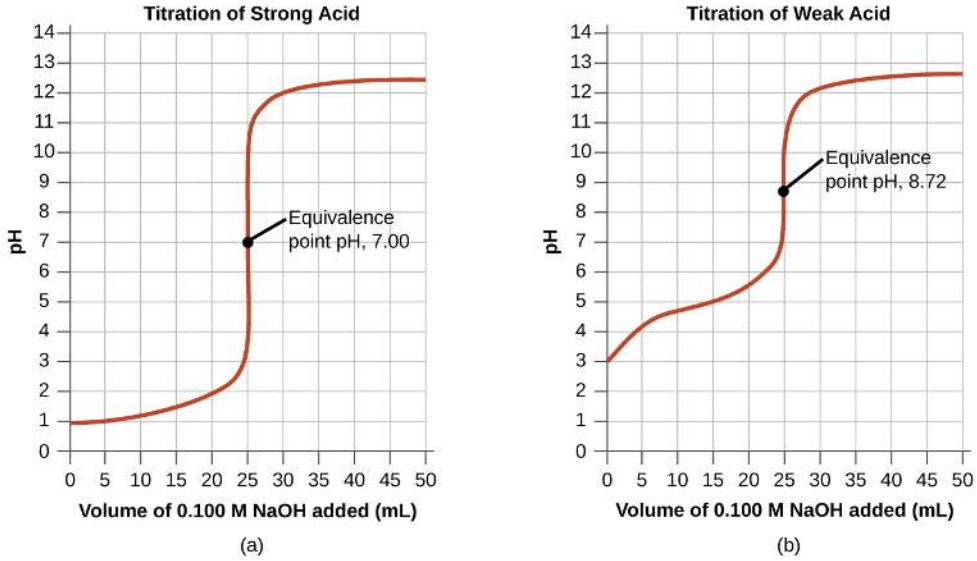


Figure **3.7.1**: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence point of 8.72 pH.

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

The titration of a weak acid with a strong base (or of a weak base with a strong acid) is somewhat more complicated than that just discussed, but it follows the same general principles. Let us consider the titration of 25.0 mL of 0.100 *M* acetic acid (a weak acid) with 0.100 *M* sodium hydroxide and compare the titration curve with that of the strong acid. Table **3.7.1** gives the pH values during the titration, Figure **3.7.1*b*** shows the titration curve.

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

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

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

Example **3.7.2**: Titration of a Weak Acid with a Strong Base

The titration curve shown in Figure **3.7.1*b*** is for the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

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

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

Solution

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

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]} \approx \frac{[H3O+]^2}{[CH3CO2H]_0}$$

and

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

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

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

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

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

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

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

$$K_b = \frac{[CH3CO2H][OH-]}{[CH3CO2-]}$$

$$K_a = \frac{[CH3CO2-][H+]}{[CH3CO2H]}, \text{ so } \frac{[CH3CO2H]}{[CH3CO2-]} = \frac{[H^+]}{K_a}.$$

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

$$K_b = \frac{[H^+][OH^-]}{K_a} \tag{3.7.2}$$

$$= \frac{K_w}{K_a} \tag{3.7.3}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \tag{3.7.4}$$

$$= 5.6 \times 10^{-10} \tag{3.7.5}$$

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

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

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

$$pH = 14.00 - 5.28 = 8.72$$

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

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

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

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[Base]}{[Acid]} = -\log(K_a) + \log\frac{[CH3CO2-]}{[CH3CO2H]} = -\log(1.8\times10^{-5}) + \log(1)$$

(as the concentrations of $\mathbf{CH_3CO_2^-}$ and CH_3CO_2H are the same)

Thus:

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

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

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

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

So:

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

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

? Exercise 3.7.2

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

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

Answer a

0.00 mL: 2.37

Answer b

15.0 mL: 3.92

Answer c

25.00 mL: 8.29

Answer d

30.0 mL: 12.097

Acid-Base Indicators

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

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

$$\underbrace{\mathrm{HIn\,(aq)}}_{\text{red}} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \underbrace{\mathrm{In^-\,(aq)}}_{\text{yellow}}$$

$$K_a = \frac{[H3O+][In-]}{[HIn]} = 4.0 \times 10^{-4}$$

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

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

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{3.7.6}$$

Equation 3.7.6 shows us how the ratio of $\frac{[In-]}{[HIn]}$ varies with the concentration of hydronium ion. The above expression describing the indicator equilibrium can be rearranged:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{3.7.7}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{3.7.8}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{3.7.9}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{3.7.10}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{3.7.11}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{3.7.12}$$

Equation 3.7.12 is the same as the *Henderson-Hasselbalch equation*, which can be used to describe the equilibrium of indicators.

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

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure **3.7.2** presents several indicators, their colors, and their color-change intervals.

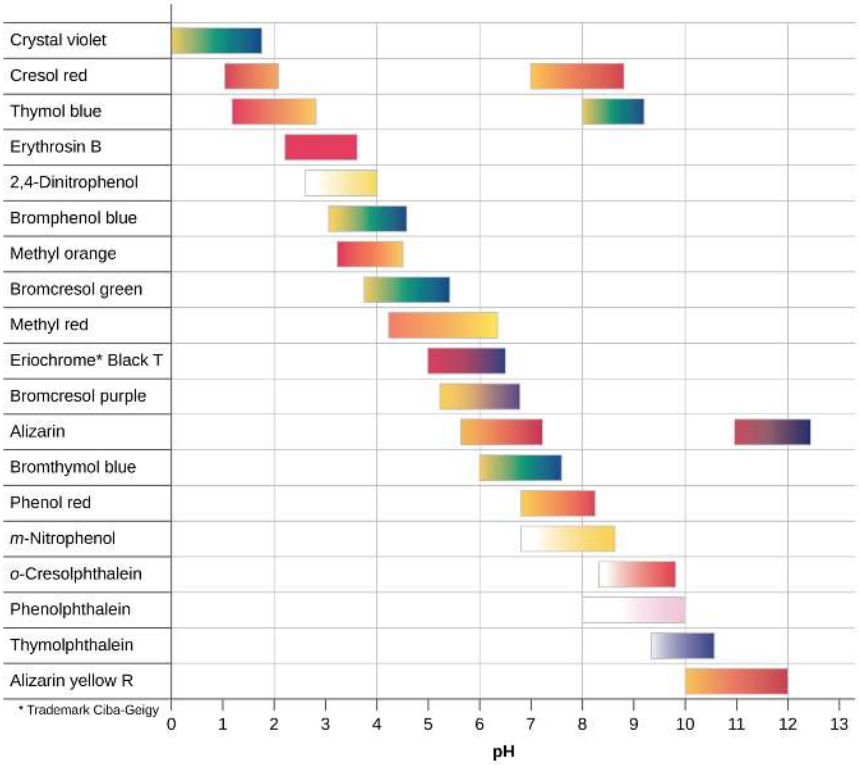


Figure **3.7.2**: This chart illustrates the ranges of color change for several acid-base indicators.

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

The color change intervals of three indicators are shown in Figure **3.7.3**. The equivalence points of both the titration of the strong acid and of the weak acid are located in the color-change interval of phenolphthalein. We can use it for titrations of either strong acid with strong base or weak acid with strong base.

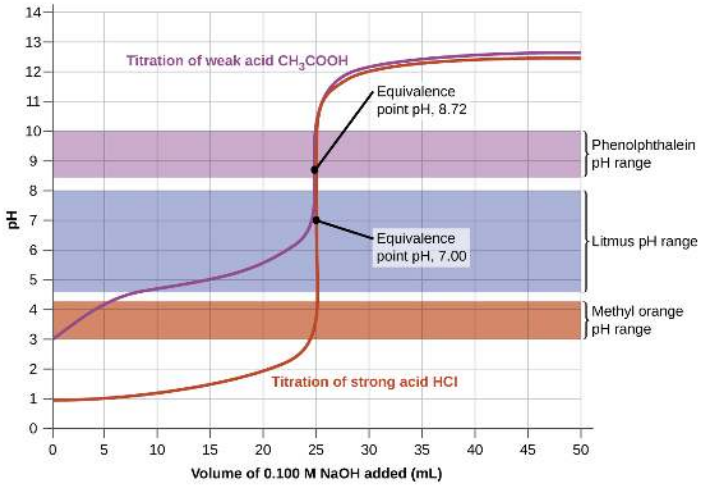


Figure **3.7.3**: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and methyl orange are indicated by the shaded areas.

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

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

We could use methyl orange for the HCl titration, but it would not give very accurate results: (1) It completes its color change slightly before the equivalence point is reached (but very close to it, so this is not too serious); (2) it changes color, as Figure **3.7.2** demonstrates, during the addition of nearly 0.5 mL of NaOH, which is not so sharp a color change as that of litmus or phenolphthalein; and (3) it goes from yellow to orange to red, making detection of a precise endpoint much more challenging than the colorless to pink change of phenolphthalein. Figure **3.7.2** shows us that methyl orange would be completely useless as an indicator for the CH_3CO_2H titration. Its color change begins after about 1 mL of NaOH has been added and ends when about 8 mL has been added. The color change is completed long before the equivalence point (which occurs when 25.0 mL of NaOH has been added) is reached and hence provides no indication of the equivalence point.

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

Summary

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

Glossary

acid-base indicator

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

color-change interval

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

titration curve

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

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3.E: Acid-Base Equilibria (Exercises)

14.1: Brønsted-Lowry Acids and Bases

Q14.1.1

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

S14.1.1

One example for NH_3 as a conjugate acid: $\mathbf{NH_2^- + H^+ \longrightarrow NH_3}$; as a conjugate base: $\mathbf{NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)}$

Q14.1.2

Write equations that show $\mathbf{H_2PO_4^-}$ acting both as an acid and as a base.

Q14.1.3

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. $\mathbf{H_3O^+}$
b. HCl
c. NH_3
d. CH_3CO_2H
e. $\mathbf{NH_4^+}$
f. $\mathbf{HSO_4^-}$

S14.1.3

a. $\mathbf{H_3O^+(aq) \longrightarrow H^+(aq) + H_2O_{(l)}}$;
b. $\mathbf{HCl(l) \longrightarrow H^+(aq) + Cl^-(aq)}$;
c. $\mathbf{NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq)}$;
d. $\mathbf{CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq)}$;
e. $\mathbf{NH_4^+(aq) \longrightarrow H^+(aq) + NH_3(aq)}$;
f. $\mathbf{HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)}$

Q14.1.4

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

a. HNO_3
b. $\mathbf{PH_4^+}$
c. H_2S
d. CH_3CH_2COOH
e. $\mathbf{H_2PO_4^-}$
f. HS^-

Q14.1.5

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. H_2O
b. $\mathbf{OH^-}$
c. NH_3
d. CN^-
e. S^{2-}
f. $\mathbf{H_2PO_4^-}$

S14.1.5

a. $\mathbf{H_2O_{(l)} + H^+(aq) \longrightarrow H_3O^+(aq)}$
b. $\mathbf{OH^-(aq) + H^+(aq) \longrightarrow H_2O_{(l)}}$
c. $\mathbf{NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)}$;
d. $\mathbf{CN^-(aq) + H^+(aq) \longrightarrow HCN(aq)}$
e. $\mathbf{S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq)}$
f. $\mathbf{H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)}$

Q14.1.6

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

a. HS^-
b. $\mathbf{PO_4^{3-}}$
c. $\mathbf{NH_2^-}$
d. C_2H_5OH
e. O^{2-}
f. $\mathbf{H_2PO_4^-}$

Q14.1.7

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. $\mathbf{OH^-}$
b. H_2O
c. $\mathbf{HCO_3^-}$
d. NH_3
e. $\mathbf{HSO_4^-}$
f. H_2O_2
g. HS^-
h. $\mathbf{H_5N_2^+}$

S14.1.7

H_2O, O^{2-}; H_3O^+, $\mathbf{OH^-}$; H_2CO_3, $\mathbf{CO_3^{2-}}$; $\mathbf{NH_4^+}$, $\mathbf{NH_2^-}$; H_2SO_4, $\mathbf{SO_4^{2-}}$; $\mathbf{H_3O_2^+}$, $\mathbf{HO_2^-}$; H_2S; S^{2-}; $\mathbf{H_6N_2^{2+}}$, H_4N_2

Q14.1.8

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. H_2S
b. $\mathbf{H_2PO_4^-}$
c. PH_3
d. HS^-
e. $\mathbf{HSO_3^-}$
f. $\mathbf{H_3O_2^+}$
g. H_4N_2
h. CH_3OH

Q14.1.9

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $\mathbf{HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-}$
b. $\mathbf{CN^- + H_2O \longrightarrow HCN + OH^-}$
c. $\mathbf{H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-}$
d. $\mathbf{HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O}$

e. $O^{2-} + H_2O \longrightarrow 2\,OH^-$
f. $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$
g. $H_2S + NH_2^- \longrightarrow HS^- + NH_3$

S14.1.9

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA. HNO_3(BA), H_2O(BB), H_3O^+(CA), **NO_3^- (CB)**; CN^-(BB), H_2O(BA), HCN(CA), **OH^-** (CB); H_2SO_4(BA), Cl^-(BB), HCl(CA), **HSO_4^- (CB)**; **HSO_4^- (BA)**, OH^-(BB), **SO_4^{2-} (CB)**, H_2O(CA); O^{2-}(BB), H2O(BA) **OH^-** (CB and CA); $[Cu(H_2O)_3(OH)]^+$(BB), $[Al(H_2O)_6]^{3+}$(BA), $[Cu(H_2O)_4]^{2+}$(CA), $[Al(H_2O)_5(OH)]^{2+}$(CB); H_2S(BA), **NH_2^- (BB)**, HS^-(CB), NH_3(CA)

Q14.1.10

Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
b. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
c. $HS^- + H_2O \longrightarrow H_2S + OH^-$
d. $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
e. $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$
f. $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$
g. $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

Q14.1.11

What are amphiprotic species? Illustrate with suitable equations.

S14.1.11

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O.

- As an acid: $H_2O(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$.
- As a base: $H_2O(aq) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Q14.1.12

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

a. H_2O
b. $H_2PO_4^-$
c. S^{2-}
d. CO_3^{2-}
e. HSO_4^-

Q14.1.13

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

a. NH_3
b. HPO_4^-
c. Br^-
d. NH_4^+
e. ASO_4^{3-}

S14.113

amphiprotic: $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$, $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$; $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-$; not amphiprotic: Br^-; NH_4^+; AsO_4^{3-}

Q14.1.14

Is the self ionization of water endothermic or exothermic? The ionization constant for water (K_w) is $\mathbf{2.9 \times 10^{-14}}$ at 40 °C and $\mathbf{9.6 \times 10^{-14}}$ at 60 °C.

14.2: pH and pOH

Q14.2.1

Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9×10^{-14} at 40 °C.

S14.2.1

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C,

$[H_3O^+] = [OH^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}$.

Q14.2.2

The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

Q14.2.3

The ionization constant for water (K_w) is 9.614×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

S14.2.3

x = 3.101×10^{-7} M = $[H_3O^+] = [OH^-]$

pH = -log 3.101×10^{-7} = −(−6.5085) = 6.5085

pOH = pH = 6.5085

Q14.2.4

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.200 *M* HCl
b. 0.0143 *M* NaOH
c. 3.0 *M* HNO_3
d. 0.0031 *M* $Ca(OH)_2$

Q14.2.5

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.000259 *M* $HClO_4$
b. 0.21 *M* NaOH
c. 0.000071 *M* $Ba(OH)_2$
d. 2.5 *M* KOH

S14.2.5

pH = 3.587; pOH = 10.413; pH = 0.68; pOH = 13.32; pOH = 3.85; pH = 10.15; pH = −0.40; pOH = 14.4

Q14.2.6

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

Q14.2.6

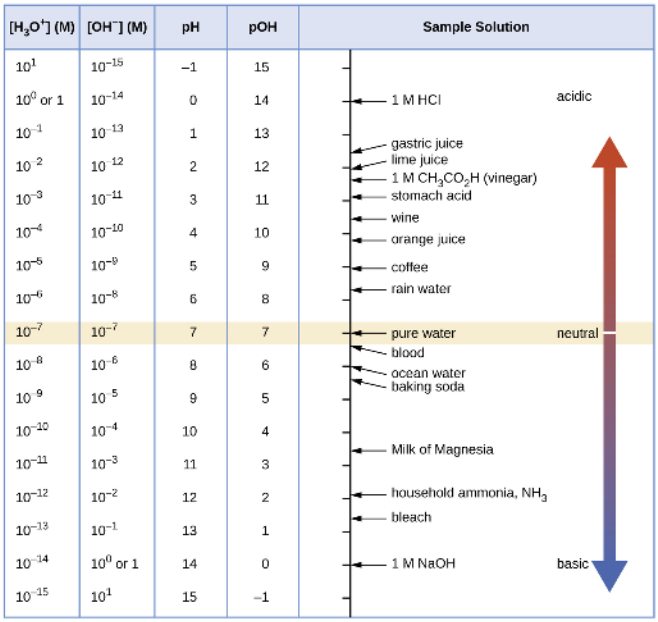
What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

S14.2.6

$[H_3O^+] = 3.0 \times 10^{-7}$ *M*; $[OH^-] = 3.3 \times 10^{-8}$ *M*

Q14.2.7

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See below Figure for useful information.



Q14.2.8

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure for useful information.

S14.2.9

$[H_3O^+] = 1 \times 10^{-2}\ M$; $[OH^-] = 1 \times 10^{-12}\ M$

Q14.2.9

The hydronium ion concentration in a sample of rainwater is found to be $1.7 \times 10^{-6}\ M$ at 25 °C. What is the concentration of hydroxide ions in the rainwater?

Q14.2.10

The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3}\ M$ at 25 °C. What is the concentration of hydronium ions in the solution?

S14.2.10

$[OH^-] = 3.1 \times 10^{-12}\ M$

14.3: Relative Strengths of Acids and Bases

Q14.3.1

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

Q14.3.2

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

Q14.3.3

Use this list of important industrial compounds (and Figure) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

a. Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.
b. List those compounds in that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
c. List those compounds in that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

Q14.3.4

The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

S14.3.4

$[H_2O] > [CH_3CO_2H] > [\mathbf{H_3O^+}] \approx [\mathbf{CH_3CO_2^-}] > [OH^-]$

Q14.3.5

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

Q14.3.4

Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

S14.3.4

The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

Q14.3.7

Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

Q14.3.8

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

S14.3.8

$$\underset{\text{BB}}{\mathbf{Mg(OH)_2}(s)} + \underset{\text{BA}}{\mathbf{HCl}(aq)} \longrightarrow \underset{\text{CB}}{\mathbf{Mg^{2+}}(aq)} + 2\,\underset{\text{CA}}{\mathbf{Cl^-}}(aq) + 2\,\mathbf{H_2O}(l)$$

Q14.3.9

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

Q14.3.10

What is the ionization constant at 25 °C for the weak acid $\mathbf{CH_3NH_3^+}$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

S14.3.10

$\boldsymbol{K_a = 2.3 \times 10^{-11}}$

Q14.3.11

What is the ionization constant at 25 °C for the weak acid $\mathbf{(CH_3)_2NH_2^+}$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 7.4 \times 10^{-4}$?

Q14.3.12

Which base, CH_3NH_2 or $(CH_3)_2NH$, is the strongest base? Which conjugate acid, $\mathbf{(CH_3)_2NH_2^+}$ or $(CH_3)_2NH$, is the strongest acid?

S14.3.12

The strongest base or strongest acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $\mathbf{CH_3NH_3^+}$.

Q14.3.3

Which is the stronger acid, $\mathbf{NH_4^+}$ or HBrO?

Q14.3.14

Which is the stronger base, $(CH_3)_3N$ or $\mathbf{H_2BO_3^-}$?

S14.3.14

triethylamine.

Q14.3.15

Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

a. H_2O or HF
b. $B(OH)_3$ or $Al(OH)_3$
c. $\mathbf{HSO_3^-}$ or $\mathbf{HSO_4^-}$
d. NH_3 or H_2S
e. H_2O or H_2Te

Q14.3.16

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

a. $\mathbf{HSO_4^-}$ or $\mathbf{HSeO_4^-}$
b. NH_3 or H_2O
c. PH_3 or HI
d. NH_3 or PH_3
e. H_2S or HBr

S14.3.16

a. $\mathbf{HSO_4^-}$; higher electronegativity of the central ion. H_2O;
b. NH_3 is a base and water is neutral, or decide on the basis of K_a values. HI;
c. PH_3 is weaker than HCl; HCl is weaker than HI. Thus, PH_3 is weaker than HI.
d. PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group.
e. HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S, so HBr is the stronger acid.

Q14.3.17

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: HCl, HBr, HI
b. basicity: H_2O, OH^-, H^-, Cl^-
c. basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$).
d. acidity: HF, H_2O, NH_3, CH_4

Q14.3.18

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

a. acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$
b. basicity: $\mathbf{BrO_2^-}$, $\mathbf{ClO_2^-}$, $\mathbf{IO_2^-}$
c. acidity: HOCl, HOBr, HOI
d. acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
e. basicity: $\mathbf{NH_2^-}$, HS^-, HTe^-, $\mathbf{PH_2^-}$
f. basicity: BrO^-, $\mathbf{BrO_2^-}$, $\mathbf{BrO_3^-}$, $\mathbf{BrO_4^-}$

S14.3.18

a. $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element—S, in this case—forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner.
b. $\mathbf{ClO_2^- < BrO_2^- < IO_2^-}$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
c. HOI < HOBr < HOCl; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. Cl is more electronegative than Br, and I is the least electronegative of the three.
d. HOCl < HOClO < $HOClO_2$ < $HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases).
e. $\mathbf{HTe^- < HS^- \ll PH_2^- < NH_2^-}$; $\mathbf{PH_2^-}$ and $\mathbf{NH_2^-}$ are anions of weak bases, so they act as strong bases toward H^+. $\mathbf{HTe^-}$ and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion.
f. $\mathbf{BrO_4^- < BrO_3^- < BrO_2^- < BrO^-}$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

Q14.3.19

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base? See Table.

Q14.3.20

The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

$$\mathbf{[H_2O] > [C_6H_4OH(CO_2H)] > [H^+]_0 > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]}$$

What do we represent when we write:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq)? \tag{3.E.1}$$

Q14.3.21

Explain why equilibrium calculations are not necessary to determine ionic concentrations in solutions of certain strong electrolytes such as NaOH and HCl. Under what conditions are equilibrium calculations necessary as part of the determination of the concentrations of all ions of some other strong electrolytes in solution?

S14.3.21

Strong electrolytes are 100% ionized, and, as long as the component ions are neither weak acids nor weak bases, the ionic species present result from the dissociation of the strong electrolyte. Equilibrium calculations are necessary when one (or more) of the ions is a weak acid or a weak base.

Q14.3.22

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

Q14.3.23

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

S14.3.23

1. Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration.
2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

Q14.3.24

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?

Q14.3.25

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water (Hint: Use LeChâtelier's principle.)?

a. addition of NaOH
b. addition of HCl
c. addition of NH_4Cl

S14.3.25

The addition of HCl

Q14.3.26

Which of the following will increase the percent of HF that is converted to the fluoride ion in water?

a. addition of NaOH
b. addition of HCl
c. addition of NaF

Q14.3.27

What is the effect on the concentrations of $\mathbf{NO_2^-}$, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

a. HCl
b. HNO_2
c. NaOH
d. NaCl
e. KNO

The equation for the equilibrium is:

$$\mathbf{NO_2^-}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{HNO_2}(aq) + \mathbf{OH^-}(aq) \tag{3.E.2}$$

S14.3.27

a. Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of $\mathbf{NO_2^-}$ ions.
b. Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of $\mathbf{NO_2^-}$ ions and decreasing the concentration of OH^- ions.
c. Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of $\mathbf{NO_2^-}$ ions and decreasing the concentrations of HNO_2.
d. Adding NaCl has no effect on the concentrations of the ions.

e. Adding KNO_2 adds $\mathbf{NO_2^-}$ ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

Q14.3.28

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

a. HCl
b. KF
c. NaCl
d. KOH
e. HF

The equation for the equilibrium is:

$$\mathbf{HF}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{F^-}(aq) \tag{3.E.3}$$

Q14.3.29

Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

S14.3.29

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

Q14.3.30

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

CH_3CO_2H: $\mathbf{[H_3O^+]} = 1.34 \times 10^{-3}$ *M*;

$\mathbf{[CH_3CO_2^-]} = 1.34 \times 10^{-3}$ *M*;

$[CH_3CO_2H] = 9.866 \times 10^{-2}$ *M*;

ClO^-: $[OH^-] = 4.0 \times 10^{-4}$ *M*;

$[HClO] = 2.38 \times 10^{-5}$ *M*;

$[ClO^-] = 0.273$ *M*;

HCO_2H: $[HCO_2H] = 0.524$ *M*;

$\mathbf{[H_3O^+]} = 9.8 \times 10^{-3}$ *M*; $\mathbf{[HCO_2^-]} = 9.8 \times 10^{-3}$ *M*;

$\mathbf{C_6H_5NH_3^+}$: $\mathbf{[C_6H_5NH_3^+]} = 0.233$ *M*;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}$ *M*;

$\mathbf{[H_3O^+]} = 2.3 \times 10^{-3}$ *M*

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;

$\mathbf{[NH_4^+]} = 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

HNO_2: $\mathbf{[H_3O^+]} = 0.011$ *M*;

$\mathbf{[NO_2^-]} = 0.0438$ *M*;

$[HNO_2] = 1.07$ *M*;

$(CH_3)_3N$: $[(CH_3)_3N] = 0.25\ M$;

$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}\ M$;

$[OH^-] = 4.3 \times 10^{-3}\ M$;

$\mathbf{NH_4^+}$: $[\mathbf{NH_4^+}] = 0.100\ M$;

$[NH_3] = 7.5 \times 10^{-6}\ M$;

$[H_3O^+] = 7.5 \times 10^{-6}\ M$

a. $\boldsymbol{K_b = 1.8 \times 10^{-5}}$;
b. $\boldsymbol{K_a = 4.5 \times 10^{-4}}$;
c. $\boldsymbol{K_b = 7.4 \times 10^{-5}}$;
d. $\boldsymbol{K_a = 5.6 \times 10^{-10}}$

Q14.3.31

Determine K_b for the nitrite ion, $\mathbf{NO_2^-}$. In a 0.10-*M* solution this base is 0.0015% ionized.

Q14.3.32

Determine K_a for hydrogen sulfate ion, $\mathbf{HSO_4^-}$. In a 0.10-*M* solution the acid is 29% ionized.

S14.3.32

$\boldsymbol{K_a = 1.2 \times 10^{-2}}$

Q14.3.33

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

a. F^-
b. $\mathbf{NH_4^+}$
c. $\mathbf{AsO_4^{3-}}$
d. $\mathbf{(CH_3)_2NH_2^+}$
e. $\mathbf{NO_2^-}$
f. $\mathbf{HC_2O_4^-}$ (as a base)

Q14.3.52

Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

1. HTe^- (as a base)
2. $\mathbf{(CH_3)_3NH^+}$
3. $\mathbf{HAsO_4^{3-}}$ (as a base)
4. $\mathbf{HO_2^-}$ (as a base)
5. $\mathbf{C_6H_5NH_3^+}$
6. $\mathbf{HSO_3^-}$ (as a base)

S14.3.52

a. $\boldsymbol{K_b = 4.3 \times 10^{-12}}$;
b. $\boldsymbol{K_a = 1.4 \times 10^{-10}}$;
c. $\boldsymbol{K_b = 1 \times 10^{-7}}$;
d. $\boldsymbol{K_b = 4.2 \times 10^{-3}}$;
e. $\boldsymbol{K_b = 4.2 \times 10^{-3}}$;
f. $\boldsymbol{K_b = 8.3 \times 10^{-13}}$

Q14.3.53

For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?

a. 3×10^{-8} *M* HNO_3
b. 0.10 g HCl in 1.0 L of solution
c. 0.00080 g NaOH in 0.50 L of solution
d. 1×10^{-7} *M* $Ca(OH)_2$
e. 0.0245 *M* KNO_3

Q14.3.54

Even though both NH_3 and $C_6H_5NH_2$ are weak bases, NH_3 is a much stronger acid than $C_6H_5NH_2$. Which of the following is correct at equilibrium for a solution that is initially 0.10 *M* in NH_3 and 0.10 *M* in $C_6H_5NH_2$?

a. $[OH^-] = [NH_4^+]$
b. $[NH_4^+] = [C_6H_5NH_3^+]$
c. $[OH^-] = [C_6H_5NH_3^+]$
d. $[NH_3] = [C_6H_5NH_2]$
e. both a and b are correct

is the correct statement.

Q14.3.55

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.25 *M* in HCO_2H and 0.10 *M* in HClO.

Q14.3.56

Calculate the equilibrium concentration of the nonionized acids and all ions in a solution that is 0.134 *M* in HNO_2 and 0.120 *M* in HBrO.

S14.3.56

$[H_3O^+] = 7.5 \times 10^{-3}$ *M*

$[HNO_2] = 0.126$ $[OH^-] = 1.3 \times 10^{-12}$ *M* $[BrO^-] = 3.2 \times 10^{-8}$ *M* $[HBrO] = 0.120$ *M*

Q14.3.57

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.25 *M* in CH_3NH_2 and 0.10 *M* in C_5H_5N ($K_b = 1.7 \times 10^{-9}$).

Q14.3.58

Calculate the equilibrium concentration of the nonionized bases and all ions in a solution that is 0.115 *M* in NH_3 and 0.100 *M* in $C_6H_5NH_2$.

S14.3.58

$[OH^-] = [NO_4^+] = 0.0014$ *M*

$[NH_3] = 0.144$ *M* $[H_3O^+] = 6.9 \times 10^{-12}$ *M* $[C_6H_5NH_3^+] = 3.9 \times 10^{-8}$ *M* $[C_6H_5NH_2] = 0.100$ *M*

Q14.3.59

Using the K_a values in Appendix H, place $Al(H_2O)_6^{3+}$ in the correct location in Figure.

Q14.3.60

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in Appendix H and Appendix I.

a. 0.0092 *M* HClO, a weak acid
b. 0.0784 *M* $C_6H_5NH_2$, a weak base
c. 0.0810 *M* HCN, a weak acid
d. 0.11 *M* $(CH_3)_3N$, a weak base
e. 0.120 *M* $\mathbf{Fe(H_2O)_6^{2+}}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

S14.3.60

$$\frac{[H3O+][ClO-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 3.5 \times 10^{-8}$$

Solving for *x* gives 1.79×10^{-5} *M*. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO] = 1.8 \times 10^{-5}$ *M*[HClO] = 0.00092 *M* $[OH^-] = 5.6 \times 10^{-10}$ *M*;

$$\frac{[C6H5NH3+][OH-]}{[C6H5NH2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.6 \times 10^{-10}$$

Solving for *x* gives 6.01×10^{-6} *M*.

This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $\mathbf{[CH_3CO_2^-]}$ = $[OH^-] = 6.0 \times 10^{-6}$ *M* $[C_6H_5NH_2] = 0.00784$ $[H_3O^+] = 1.7\times 10^{-9}$ *M*; $\frac{[H3O+][CN-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$ Solving for *x* gives 5.69×10^{-6} *M*. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[H_3O^+] = [CN^-] = 5.7 \times 10^{-6}$ *M* [HCN] = 0.0810 *M* $[OH^-] = 1.8 \times 10^{-9}$ *M*; $\frac{[(CH3)3NH+][OH-]}{[(CH3)3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 7.4 \times 10^{-5}$ Solving for *x* gives 2.85×10^{-3} *M*. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[(CH_3)_3NH^+] = [OH^-] = 2.9 \times 10^{-3}$ *M* $[(CH_3)_3N] = 0.11$ *M* $[H_3O^+] = 3.5 \times 10^{-12}$ *M*; $\frac{[Fe(H2O)5(OH)+][H3O+]}{[Fe(H2O)6^2+]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$ Solving for *x* gives 1.39×10^{-4} *M*. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}$ *M* $\mathbf{[Fe(H_2O)_6^{2+}]} = 0.120$ *M* $[OH^-] = 7.2 \times 10^{-11}$ *M*

Q14.3.61

Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the hydronium ion concentration in a 0.698-*M* solution of $C_2H_5CO_2H$?

Q14.3.62

White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

S14.3.62

pH = 2.41

Q14.3.63

The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

Q14.3.64

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

S14.3.64

$[C_{10}H_{14}N_2] = 0.049$ *M*

$[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}$ *M* $\mathbf{[C_{10}H_{14}N_2H_2^{2+}]} = 1.4 \times 10^{-11}$ *M* $[OH^-] = 1.9 \times 10^{-4}$ *M* $[H_3O^+] = 5.3 \times 10^{-11}$ *M*

Q14.3.65

The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.

Q14.3.66

The pH of a 0.15-*M* solution of $\mathbf{HSO_4^-}$ is 1.43. Determine K_a for $\mathbf{HSO_4^-}$ from these data.

S14.3.66

$\boldsymbol{K_a = 1.2 \times 10^{-2}}$

Q14.3.67

The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:

$$\mathbf{C_8H_{10}N_4O_2}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{C_8H_{10}N_4O_2H^+}(aq) + \mathbf{OH^-}(aq)$$

Q14.3.68

The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

S14.3.68

$\boldsymbol{K_b = 1.77 \times 10^{-5}}$

14.4: Hydrolysis of Salt Solutions

Q14.4.1

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $Al(NO_3)_3$
b. RbI
c. $KHCO_2$
d. CH_3NH_3Br

Q14.4.2

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $FeCl_3$
b. K_2CO_3
c. NH_4Br
d. $KClO_4$

S14.4.2

acidic; basic; acidic; neutral

Q14.4.3

Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

14.5: Polyprotic Acids

Q15.5.1

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid:

- $\mathbf{[H_3O^+]}$,
- $[\boldsymbol{OH^-}]$
- $[\boldsymbol{H_2CO_3}]$

- $[HCO_3^-]$
- $[CO_3^{2-}]$

No calculations are needed to answer this question.

S15.5.1

$[H_3O^+]$ and $[HCO_3^-]$ are equal, H_3O^+ and HCO_3^- are practically equal

Q15.5.2

Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

Q15.5.3

Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

S15.5.3

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \quad K_a = 1.1 \times 10^{-3}$$

$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2^{2-}(aq) \quad K_a = 3.9 \times 10^{-6}$$

$[C_6H_4(CO_2H)_2]$ 7.2×10^{-3} *M*, $[C_6H_4(CO_2H)(CO_2)^-] = [H_3O^+]$ 2.8×10^{-3} *M*, $[C_6H_4(CO_2)_2^{2-}]$ 3.9×10^{-6} *M*, $[OH^-]$ 3.6×10^{-12} *M*

Q15.5.4

Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

1. Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).
2. Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).
3. Under some conditions, aspirin reacts with water and forms a solution of salicylic acid and acetic acid:

$$CH_3CO_2C_6H_4CO_2H(aq) + H_2O(l) \longrightarrow HOC_6H_4CO_2H(aq) + CH_3CO_2H(aq) \tag{3.E.4}$$

   i. Which of the acids salicylic acid or acetic acid produces more hydronium ions in solution such a solution?
   ii. What are the concentrations of molecules and ions in a solution produced by the hydrolysis of 0.50 g of aspirin dissolved in enough water to give 75 mL of solution?

Q15.5.5

The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

a. What is K_a for the acid reaction of HTe^- with H_2O?
b. What is K_b for the reaction in which HTe^- functions as a base in water?
c. Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

S15.5.5

a. $K_{a2} = 1 \times 10^{-5}$;
b. $K_b = 4.3 \times 10^{-12}$;
c. $\frac{[Te^{2-}][H3O+]}{[HTe-]} = \frac{(x)(0.0141 + x)}{(0.0141 - x)} \approx \frac{(x)(0.0141)}{0.0141} = 1 \times 10^{-5}$. Solving for *x* gives 1×10^{-5} *M*. Therefore, compared with 0.014 *M*, this value is negligible (0.071%).

14.6: Buffers

Q14.6.1

Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

Q14.6.2

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

S14.6.2

Excess H_3O^+ is removed primarily by the reaction:

$\mathbf{H_3O^+(aq) + H_2PO_4^-(aq) \longrightarrow H_3PO_4(aq) + H_2O(l)}$ Excess base is removed by the reaction: $\mathbf{OH^-(aq) + H_3PO_4(aq) \longrightarrow H_2PO_4^-(aq) + H_2O(l)}$

Q14.6.3

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

Q14.6.4

What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$\mathbf{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}}$

S14.6.4

$[H_3O^+] = 1.5 \times 10^{-4}\ M$

Q14.6.5

What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

S14.6.6

$\mathbf{HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \quad K_a = 4.5 \times 10^{-5}}$

Q14.6.6

What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

S14.6.6

$\mathbf{CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \quad K_b = 4.4 \times 10^{-4}}$

$[OH^-] = 4.2 \times 10^{-4}\ M$

Q14.6.7

What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

S14.6.7

$\mathbf{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = 1.8 \times 10^{-5}}$

Q14.6.8

What concentration of NH_4NO_3 is required to make $[OH^-] = 1.0 \times 10^{-5}$ in a 0.200-*M* solution of NH_3?

S14.6.8

$[NH_4NO_3] = 0.36\ M$

Q14.6.9A

What concentration of NaF is required to make $[H_3O^+] = 2.3 \times 10^{-4}$ in a 0.300-*M* solution of HF?

Q14.6.9B

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

a. HCl
b. KCH_3CO_2
c. NaCl
d. KOH
e. CH_3CO_2H

S14.6.10

a. The added HCl will increase the concentration of H_3O^+ slightly, which will react with $\mathbf{CH_3CO_2^-}$ and produce CH_3CO_2H in the process. Thus, $[\mathbf{CH_3CO_2^-}]$ decreases and $[CH_3CO_2H]$ increases.
b. The added KCH_3CO_2 will increase the concentration of $[\mathbf{CH_3CO_2^-}]$ which will react with H_3O^+ and produce CH_3CO_2 H in the process. Thus, $[H_3O^+]$ decreases slightly and $[CH_3CO_2H]$ increases.
c. The added NaCl will have no effect on the concentration of the ions.
d. The added KOH will produce OH^- ions, which will react with the H_3O^+, thus reducing $[H_3O^+]$. Some additional CH_3CO_2H will dissociate, producing $[\mathbf{CH_3CO_2^-}]$ ions in the process. Thus, $[CH_3CO_2H]$ decreases slightly and $[\mathbf{CH_3CO_2^-}]$ increases.
e. The added CH_3CO_2H will increase its concentration, causing more of it to dissociate and producing more $[\mathbf{CH_3CO_2^-}]$ and H_3O^+ in the process. Thus, $[H_3O^+]$ increases slightly and $[\mathbf{CH_3CO_2^-}]$ increases.

Q14.6.11

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

a. KI
b. NH_3
c. HI
d. NaOH
e. NH_4Cl

What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

pH = 8.95

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

37 g (0.27 mol)

What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

Q14.6.1

A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

1. What is the pH of the solution?
2. Is the solution acidic or basic?

Q14.6.1

What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

a. pH = 5.222;
b. The solution is acidic. (c) pH = 5.221

Q14.6.1

A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution diluted to 0.100 L.

a. What is the pH of this buffer solution?
b. Is the solution acidic or basic?
c. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

Which acid in [link] is most appropriate for preparation of a buffer solution with a pH of 3.1? Explain your choice.

To prepare the best buffer for a weak acid HA and its salt, the ratio $\frac{[H_3O^+]}{K_a}$ should be as close to 1 as possible for effective buffer action. The $[H_3O^+]$ concentration in a buffer of pH 3.1 is $[H_3O^+] = 10^{-3.1} = 7.94 \times 10^{-4}$ *M*

We can now solve for K_a of the best acid as follows:

$$\frac{[H_3O^+]}{K_a} = 1$$

$$K_a = \frac{[H_3O^+]}{1} = 7.94 \times 10^{-4}$$

In [link], the acid with the closest K_a to 7.94×10^{-4} is HF, with a K_a of 7.2×10^{-4}.

Which acid in [link] is most appropriate for preparation of a buffer solution with a pH of 3.7? Explain your choice.

Which base in [link] is most appropriate for preparation of a buffer solution with a pH of 10.65? Explain your choice.

For buffers with pHs > 7, you should use a weak base and its salt. The most effective buffer will have a ratio $\frac{[OH^-]}{K_b}$ that is as close to 1 as possible. The pOH of the buffer is 14.00 − 10.65 = 3.35. Therefore, $[OH^-]$ is $[OH^-] = 10^{-pOH} = 10^{-3.35} = 4.467 \times 10^{-4}$ *M*.

We can now solve for K_b of the best base as follows: $\frac{[OH^-]}{K_b} = 1$ $K_b = [OH^-] = 4.47 \times 10^{-4}$ In [link], the base with the closest K_b to 4.47×10^{-4} is CH_3NH_2, with a $K_b = 4.4 \times 10^{-4}$.

Which base in [link] is most appropriate for preparation of a buffer solution with a pH of 9.20? Explain your choice.

Q14.6.4

Saccharin, $C_7H_4NSO_3H$, is a weak acid ($K_a = 2.1 \times 10^{-2}$). If 0.250 L of diet cola with a buffered pH of 5.48 was prepared from 2.00×10^{-3} g of sodium saccharide, $Na(C_7H_4NSO_3)$, what are the final concentrations of saccharine and sodium saccharide in the solution?

S14.6.4

The molar mass of sodium saccharide is 205.169 g/mol. Using the abbreviations HA for saccharin and NaA for sodium saccharide the number of moles of NaA in the solution is:

9.75×10^{-6} mol. This ionizes initially to form saccharin ions, A^-, with: $[A^-] = 3.9 \times 10^{-5}$ *M*

Q14.6.5

What is the pH of 1.000 L of a solution of 100.0 g of glutamic acid ($C_5H_9NO_4$, a diprotic acid; $K_1 = 8.5 \times 10^{-5}$, $K_2 = 3.39 \times 10^{-10}$) to which has been added 20.0 g of NaOH during the preparation of monosodium glutamate, the flavoring agent? What is the pH when exactly 1 mol of NaOH per mole of acid has been added?

14.7: Acid-Base Titrations

Q14.7.1

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

S14.7.1

At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

Q14.7.2

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

Q14.7.3

Why can we ignore the contribution of water to the concentrations of H_3O^+ in the solutions of following acids:

- 0.0092 *M* HClO, a weak acid
- 0.0810 *M* HCN, a weak acid
- 0.120 *M* $\mathbf{Fe(H_2O)_6^{2+}}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

but not the contribution of water to the concentration of OH^-?

S14.7.3

In an acid solution, the only source of OH^- ions is water. We use K_w to calculate the concentration. If the contribution from water was neglected, the concentration of OH^- would be zero.

Q14.7.4

We can ignore the contribution of water to the concentration of OH^- in a solution of the following bases:

0.0784 *M* $C_6H_5NH_2$, a weak base

0.11 *M* $(CH_3)_3N$, a weak base

but not the contribution of water to the concentration of H_3O^+?

Q14.7.5

Draw a curve for a series of solutions of HF. Plot $[H_3O^+]_{total}$ on the vertical axis and the total concentration of HF (the sum of the concentrations of both the ionized and nonionized HF molecules) on the horizontal axis. Let the total concentration of HF vary from 1×10^{-10} *M* to 1×10^{-2} *M*.



A graph is shown that is titled “Plot of [H subscript 3 O superscript +] Against [H F].” The horizontal axis is labeled “[H F], M.” The axis begins at 10 superscript negative 10 and includes markings every 10 superscript 2 units up to 1.0. The vertical axis is labeled “[H subscript 3 O superscript plus], M” and begins at 10 superscript negative 10 and increases by 10 superscript 2 up to 1.0. A black curve starts at the left side of the graph at (10 superscript negative 10, 10 superscript negative 7). The line extends horizontally to a horizontal axis value of 10 superscript negative 8. After this, the line gradually increases at a steady rate to a value just over 10 superscript negative 3 at a horizontal axis value of 10 superscript negative 2.

Q14.7.6

Draw a curve similar to that shown in Figure for a series of solutions of NH_3. Plot $[OH^-]$ on the vertical axis and the total concentration of NH_3 (both ionized and nonionized NH_3 molecules) on the horizontal axis. Let the total concentration of NH_3 vary from 1×10^{-10} *M* to 1×10^{-2} *M*.

Q14.7.7

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 *M* KOH.

1. no KOH added
2. 20 mL of KOH solution added
3. 39 mL of KOH solution added
4. 40 mL of KOH solution added
5. 41 mL of KOH solution added

S14.7.7

1. pH = 2.50;
2. pH = 4.01;
3. pH = 5.60;
4. pH = 8.35;
5. pH = 11.08

Q14.7.8

The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-M solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

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CHAPTER OVERVIEW

4: Equilibria of Other Reaction Classes

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General Chemistry

We previously learned about aqueous solutions and their importance, as well as about solubility rules. While this gives us a picture of solubility, that picture is not complete if we look at the rules alone. Solubility equilibrium, which we will explore in this chapter, is a more complex topic that allows us to determine the extent to which a slightly soluble ionic solid will dissolve, and the conditions under which precipitation.

4.1: Precipitation and Dissolution

4.2: Lewis Acids and Bases

4.3: Coupled Equilibria

4.E: Equilibria of Other Reaction Classes (Exercises)

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4.1: 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 **4.1.1**). 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:

$$\mathrm{AgCl}(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

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.

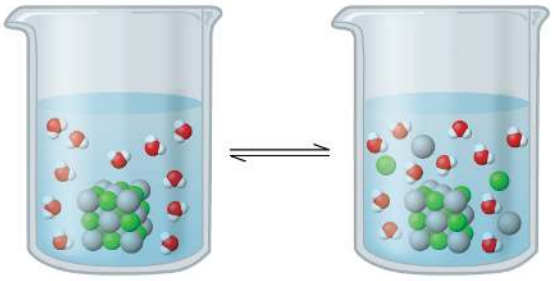


Figure **4.1.1**: Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

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 4.1.1: 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 4.1.1 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 4.1.1: 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. $\mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{I^-}(aq) \quad K_{sp} = [\mathrm{Ag^+}][\mathrm{I^-}]$
b. $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]$
c. $\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2$
d. $\mathrm{Mg(NH_4)PO_4}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + \mathrm{NH_4^+}(aq) + \mathrm{PO_4^{3-}}(aq) \quad K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{NH_4^+}][\mathrm{PO_4^{3-}}]$
e. $\mathrm{Ca_5(PO_4)_3OH}(s) \rightleftharpoons 5\,\mathrm{Ca^{2+}}(aq) + 3\,\mathrm{PO_4^{3-}}(aq) + \mathrm{OH^-}(aq) \quad K_{sp} = [\mathrm{Ca^{2+}}]^5[\mathrm{PO_4^{3-}}]^3[\mathrm{OH^-}]$

Exercise 4.1.1

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

$\mathrm{BaSO_4}(s) \rightleftharpoons \mathrm{Ba^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}]$

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 4.1.2: 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 4.1.2

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 4.1.3: 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 $7.9 \times 10^{-5}\ M$.

Exercise 4.1.3

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer

$1.2 \times 10^{-8}\ M$

Example 4.1.4: 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 8.0×10^{-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 4.1.4

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 **4.1.5** shows how to perform those unit conversions before determining the solubility product equilibrium.

Example 4.1.5: Determination of K_{sp} from Gram Solubility

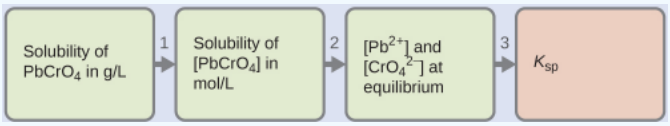
Many of the pigments used by artists in oil-based paints (Figure **4.1.2**) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product equilibrium constant for $PbCrO_4$.



Figure **4.1.2**: 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 4.1.5

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 4.1.6: Calculating the Solubility of Hg_2Cl_2

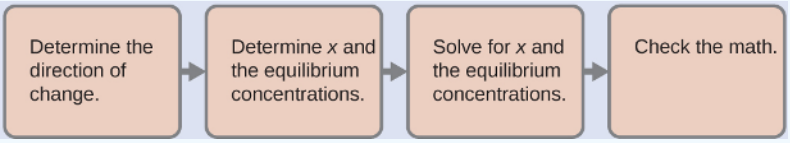
Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), Hg_2^{2+}, and chloride ions, Cl^-. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments 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 4.1.6

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 **4.1.3**).



Figure 4.1.3: 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 4.1.7 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 4.1.7: 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 4.1.7

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 4.1.8: 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 4.1.8

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 4.1.9: 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 4.1.4). 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 4.1.4: 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 4.1.9

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 4.1.8—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 4.1.10: 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 4.1.10

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 **4.1.5**). 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 **4.1.5**: 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:

$$5\,Ca^{2+} + 3\,PO_4^{3-} + OH^- \rightleftharpoons Ca_{10}(PO_4)_6 \cdot (OH)_2(s)$$

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 4.1.11: 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 4.1.11

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:

\[\ce{CH3CO2H + H2O \rightleftharpoons H3O+ + CH3CO2-}\)]

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 4.1.12: 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 ⇌	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 4.1.12

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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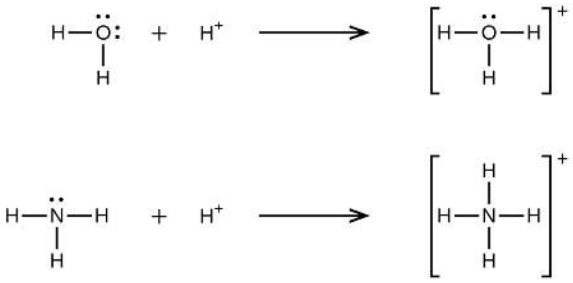
4.2: Lewis Acids and Bases

Learning Objectives

- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

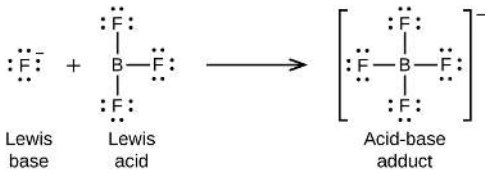
A coordinate covalent bond (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



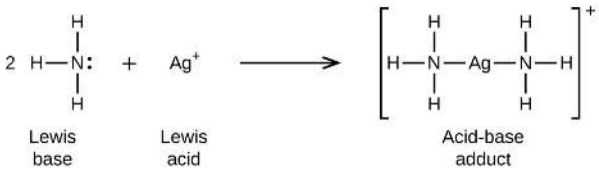
- A Lewis acid is any species (molecule or ion) that can *accept* a pair of electrons, and a Lewis base is any species (molecule or ion) that can *donate* a pair of electrons.

A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid. A **Lewis acid-base adduct**, a compound that contains a coordinate covalent bond between the Lewis acid and the Lewis base, is formed. The following equations illustrate the general application of the Lewis concept.

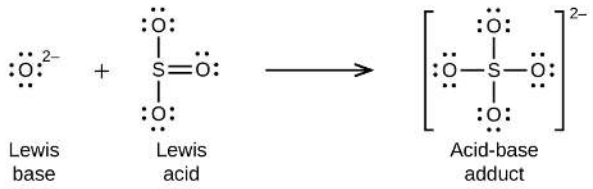
The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



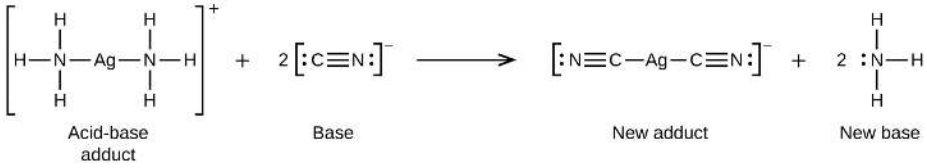
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:

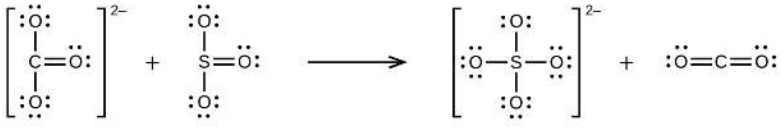


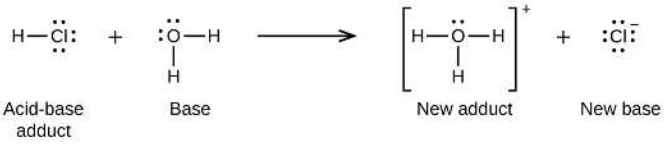
Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:



Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:

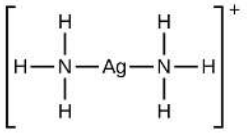






The last displacement reaction shows how the reaction of a Brønsted-Lowry acid with a base fits into the Lewis concept. A Brønsted-Lowry acid such as HCl is an acid-base adduct according to the Lewis concept, and proton transfer occurs because a more stable acid-base adduct is formed. Thus, although the definitions of acids and bases in the two theories are quite different, the theories overlap considerably.

Many slightly soluble ionic solids dissolve when the concentration of the metal ion in solution is decreased through the formation of complex (polyatomic) ions in a Lewis acid-base reaction. For example, silver chloride dissolves in a solution of ammonia because the silver ion reacts with ammonia to form the complex ion $\mathbf{Ag(NH_3)_2}^+$. The Lewis structure of the $\mathbf{Ag(NH_3)_2}^+$ ion is:



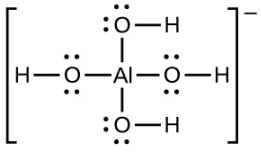
The equations for the dissolution of AgCl in a solution of NH_3 are:

$$\mathbf{AgCl}(s) \longrightarrow \mathbf{Ag}^+(aq) + \mathbf{Cl}^-(aq)$$

$$\mathbf{Ag}^+(aq) + 2\,\mathbf{NH_3}(aq) \longrightarrow \mathbf{Ag(NH_3)_2}^+(aq)$$

$$\text{Net: } \mathbf{AgCl}(s) + 2\,\mathbf{NH_3}(aq) \longrightarrow \mathbf{Ag(NH_3)_2}^+(aq) + \mathbf{Cl}^-(aq)$$

Aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $\mathbf{Al(OH)_4}^-$. The Lewis structure of the $\mathbf{Al(OH)_4}^-$ ion is:



The equations for the dissolution are:

$$\mathrm{Al(OH)_3}(s) \longrightarrow \mathrm{Al^{3+}}(aq) + 3\,\mathrm{OH^-}(aq)$$

$$\mathrm{Al^{3+}}(aq) + 4\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Al(OH)_4^-}(aq)$$

$$\text{Net: } \mathrm{Al(OH)_3}(s) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{Al(OH)_4^-}(aq)$$

Mercury(II) sulfide dissolves in a solution of sodium sulfide because HgS reacts with the S^{2-} ion:

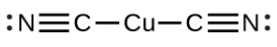
$$\mathrm{HgS}(s) \longrightarrow \mathrm{Hg^{2+}}(aq) + \mathrm{S^{2-}}(aq)$$

$$\mathrm{Hg^{2+}}(aq) + 2\,\mathrm{S^{2-}}(aq) \longrightarrow \mathrm{HgS_2^{2-}}(aq)$$

$$\text{Net: } \mathrm{HgS}(s) + \mathrm{S^{2-}}(aq) \longrightarrow \mathrm{HgS_2^{2-}}(aq)$$

A complex ion consists of a central atom, typically a transition metal cation, surrounded by ions, or molecules called ligands. These ligands can be neutral molecules like H_2O or NH_3, or ions such as CN^- or OH^-. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. The ligands aggregate themselves around the central atom, creating a new ion with a charge equal to the sum of the charges and, most often, a transitional metal ion. This more complex arrangement is why the resulting ion is called a *complex ion*. The complex ion formed in these reactions cannot be predicted; it must be determined experimentally. The types of bonds formed in complex ions are called coordinate covalent bonds, as electrons from the ligands are being shared with the central atom. Because of this, complex ions are sometimes referred to as coordination complexes. This will be studied further in upcoming chapters.

The equilibrium constant for the reaction of the components of a complex ion to form the complex ion in solution is called a formation constant (K_f) (sometimes called a stability constant). For example, the complex ion $\mathrm{Cu(CN)_2^-}$ is shown here:



It forms by the reaction:

$$\mathrm{Cu^+}(aq) + 2\,\mathrm{CN^-}(aq) \rightleftharpoons \mathrm{Cu(CN)_2^-}(aq)$$

At equilibrium:

$$K_f = Q = \frac{[Cu(CN)2-]}{[Cu+][CN-]^2}$$

The inverse of the formation constant is the dissociation constant (K_d), the equilibrium constant for the *decomposition* of a complex ion into its components in solution. We will work with dissociation constants further in the exercises for this section. Table E4 and Table **4.2.1** are tables of formation constants. In general, the larger the formation constant, the more stable the complex; however, as in the case of K_{sp} values, the stoichiometry of the compound must be considered.

Table **4.2.1**: Common Complex Ions by Decreasing Formation Constants

Substance	K_f at 25 °C
$\mathrm{[Cd(CN)_4]^{2-}}$	3×10^{18}
$\mathrm{Ag(NH_3)_2^+}$	1.7×10^{7}
$\mathrm{[AlF_6]^{3-}}$	7×10^{19}

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[Ag^+] = 1.3 \times 10^{-5}\ M$):

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

However, if NH_3 is present in the water, the complex ion, $\mathrm{Ag(NH_3)_2^+}$, can form according to the equation:

$$\mathrm{Ag^+}(aq) + 2\,\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2^+}(aq)$$

with

$$K_f = \frac{[Ag(NH3)2+]}{[Ag+][NH3]^2} = 1.7 \times 10^7$$

The large size of this formation constant indicates that most of the free silver ions produced by the dissolution of AgCl combine with NH_3 to form $\mathbf{Ag(NH_3)_2^+}$. As a consequence, the concentration of silver ions, $[Ag^+]$, is reduced, and the reaction quotient for the dissolution of silver chloride, $[Ag^+][Cl^-]$, falls below the solubility product of AgCl:

$$Q = [\mathbf{Ag^+}][\mathbf{Cl^-}] < K_{sp}$$

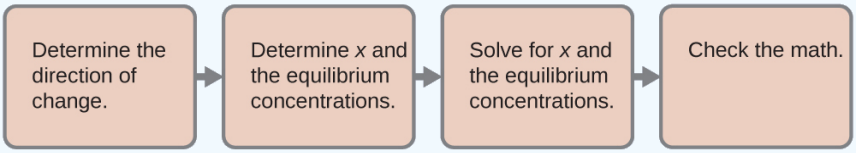
More silver chloride then dissolves. If the concentration of ammonia is great enough, all of the silver chloride dissolves.

Example 4.2.1: Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 *M* with respect to $\mathbf{Ag(NH_3)_2^+}$.

Solution

We use the familiar path to solve this problem:



1. *Determine the direction of change.* The complex ion $\mathbf{Ag(NH_3)_2^+}$ is in equilibrium with its components, as represented by the equation:

$$\mathbf{Ag^+}(aq) + 2\,\mathbf{NH_3}(aq) \rightleftharpoons \mathbf{Ag(NH_3)_2^+}(aq)$$

We write the equilibrium as a formation reaction because Table E4 lists formation constants for complex ions. Before equilibrium, the reaction quotient is larger than the equilibrium constant (K_f = 1.7 \times 10^7\), and $Q = \frac{0.10}{0 \times 0} = \infty$ (it is infinitely large), so the reaction shifts to the left to reach equilibrium.

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4.3: Coupled Equilibria

Learning Objectives

- Describe examples of systems involving two (or more) simultaneous chemical equilibria
- Calculate reactant and product concentrations for multiple equilibrium systems
- Compare dissolution and weak electrolyte formation

There are times when one equilibrium reaction does not adequately describe the system being studied. Sometimes we have more than one type of equilibrium occurring at once (for example, an acid-base reaction and a precipitation reaction).

The ocean is a unique example of a system with multiple equilibria, or multiple states of solubility equilibria working simultaneously. Carbon dioxide in the air dissolves in sea water, forming carbonic acid (H_2CO_3). The carbonic acid then ionizes to form hydrogen ions and bicarbonate ions ($\mathbf{HCO_3^-}$), which can further ionize into more hydrogen ions and carbonate ions ($\mathbf{CO_3^{2-}}$):

$$\mathbf{CO_2}(g) \rightleftharpoons \mathbf{CO_2}(aq)$$

$$\mathbf{CO_2}(aq) + \mathbf{H_2O} \rightleftharpoons \mathbf{H_2CO_3}(aq)$$

$$\mathbf{H_2CO_3}(aq) \rightleftharpoons \mathbf{H^+}(aq) + \mathbf{HCO_3^-}(aq)$$

$$\mathbf{HCO_3^-}(aq) \rightleftharpoons \mathbf{H^+}(aq) + \mathbf{CO_3^{2-}}(aq)$$

The excess H^+ ions make seawater more acidic. Increased ocean acidification can then have negative impacts on reef-building coral, as they cannot absorb the calcium carbonate they need to grow and maintain their skeletons (Figure **4.3.1**). This in turn disrupts the local biosystem that depends upon the health of the reefs for its survival. If enough local reefs are similarly affected, the disruptions to sea life can be felt globally. The world's oceans are presently in the midst of a period of intense acidification, believed to have begun in the mid-nineteenth century, and which is now accelerating at a rate faster than any change to oceanic pH in the last 20 million years.

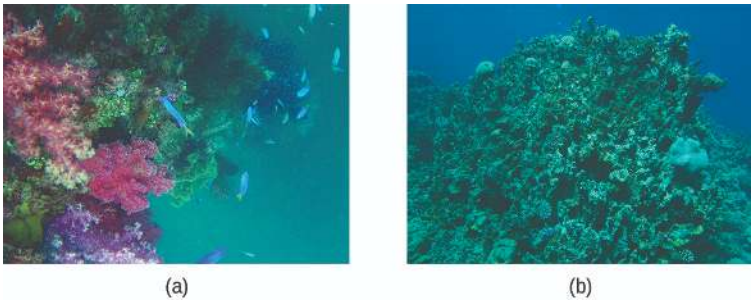


Figure **4.3.1**: Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonite skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by "prilfish"/Flickr).

> *Learn more about ocean acidification and how it affects other marine creatures.*

Slightly soluble solids derived from weak acids generally dissolve in strong acids, unless their solubility products are extremely small. For example, we can dissolve $CuCO_3$, FeS, and $Ca_3(PO_4)_2$ in HCl because their basic anions react to form weak acids (H_2CO_3, H_2S, and $\mathbf{H_2PO_4^-}$). The resulting decrease in the concentration of the anion results in a shift of the equilibrium concentrations to the right in accordance with Le Chatelier's principle.



Figure **4.3.2**: Crystal of the mineral hydroxylapatite, $Ca_5(PO_4)_3OH$, is shown here. Pure apatite is white, but like many other minerals, this sample is colored because of the presence of impurities.

Of particular relevance to us is the dissolution of hydroxylapatite, $Ca_5(PO_4)_3OH$, in acid. Apatites are a class of calcium phosphate minerals (Figure **4.3.2**); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $Ca_5(PO_4)_3OH$ and dissolved Ca^{2+}, PO_4^{3-}, and OH^- ions:

$$Ca_5(PO_4)_3OH(s) \longrightarrow 5\,Ca^{2+}(aq) + 3\,PO_4^{3-}(aq) + OH^-(aq)$$

When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:

$$PO_4^{3-}(aq) + H_3O^+ \rightleftharpoons H_2PO_4^{2-} + H_2O$$

$$PO_4^{2-}(aq) + H_3O^+ \rightleftharpoons H_2PO_4^- + H_2O$$

$$H_2PO_4^- + H_3O^+ \rightleftharpoons H_3PO_4 + H_2O$$

Hydroxide ion reacts to form water:

$$OH^-(aq) + H_3O^+ \rightleftharpoons 2\,H_2O$$

These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in an acidic solution in accord with Le Chatelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF, or stannous fluoride [more properly named tin(II) fluoride], SnF_2. They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $Ca_5(PO_4)_3F$:

$$NaF + Ca_5(PO_4)_3OH \rightleftharpoons Ca_5(PO_4)_3F + Na^+ + OH^-$$

The resulting $Ca_5(PO_4)_3F$ is slightly less soluble than $Ca_5(PO_4)_3OH$, and F^- is a weaker base than OH^-. Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $Ca_5(PO_4)_3F$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (Figure **4.3.3**).



Figure **4.3.3**: Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

$$\mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \longrightarrow \mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l)$$

Calcium hydrogen carbonate, $Ca(HCO_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

If calcium carbonate is added to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:

$$2\,\mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \longrightarrow \mathrm{H_2CO_3}(aq) + 2\,\mathrm{H_2O}(l)$$

(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:

$$\mathrm{H_2CO_3}(aq) \longrightarrow \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

Example 4.3.1: Prevention of Precipitation of $Mg(OH)_2$

Calculate the concentration of ammonium ion that is required to prevent the precipitation of $Mg(OH)_2$ in a solution with $[Mg^{2+}] = 0.10\ M$ and $[NH_3] = 0.10\ M$.

Solution

Two equilibria are involved in this system:

- Reaction (1): $\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{OH^-}(aq); \quad K_{sp} = 8.9 \times 10^{-12}$
- Reaction (2): $\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \quad K_{sp} = 1.8 \times 10^{-5}$

To prevent the formation of solid $Mg(OH)_2$, we must adjust the concentration of OH^- so that the reaction quotient for Equation (1), $Q = [Mg^{2+}][OH^-]^2$, is less than K_{sp} for $Mg(OH)_2$. (To simplify the calculation, we determine the concentration of OH^- when $Q = K_{sp}$.) $[OH^-]$ can be reduced by the addition of $\mathrm{NH_4^+}$, which shifts Reaction (2) to the left and reduces $[OH^-]$.

1. *We determine the $[OH^-]$ at which $Q = K_{sp}$ when $[Mg^{2+}] = 0.10\ M$:*

$$Q = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = (0.10)[\mathrm{OH^-}]^2 = 8.9 \times 10^{-12}$$

$$[\mathrm{OH^-}] = 9.4 \times 10^{-6}\ M$$

Solid $Mg(OH)_2$ will not form in this solution when $[OH^-]$ is less than $9.4 \times 10^{-6}\ M$.

- *We calculate the $[NH_4^+]$ needed to decrease $[OH^-]$ to $9.4 \times 10^{-6}\ M$ when $[NH_3] = 0.10$.*

$$K_b = \frac{[NH4+][OH-]}{[NH3]} = \frac{[\mathrm{NH_4^+}](9.4 \times 10^{-6})}{0.10} = 1.8 \times 10^{-5}$$

$$[\mathrm{NH_4^+}] = 0.19\ M$$

When $[NH_4^+]$ equals 0.19 *M*, $[OH^-]$ will be 9.4×10^{-6} *M*. Any $[NH_4^+]$ greater than 0.19 *M* will reduce $[OH^-]$ below 9.4×10^{-6} *M* and prevent the formation of $Mg(OH)_2$.

Exercise 4.3.1

Consider the two equilibria:

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \quad K_{sp} = 1 \times 10^{-27}$$

$$2\,H_2O(l) + H_2S(aq) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq) \quad K = 1.0 \times 10^{-26}$$

and calculate the concentration of hydronium ion required to prevent the precipitation of ZnS in a solution that is 0.050 *M* in Zn^{2+} and saturated with H_2S (0.10 *M* H_2S).

Answer

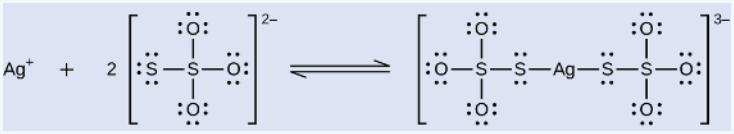
$$[H_3O^+] > 0.2\ M$$

($[S^{2-}]$ is less than 2×10^{-26} *M* and precipitation of ZnS does not occur.)

Therefore, precise calculations of the solubility of solids from the solubility product are limited to cases in which the only significant reaction occurring when the solid dissolves is the formation of its ions.

Example 4.3.2: Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($Na_2S_2O_3$, called hypo) to form the complex ion $Ag(S_2O_3)_2^{3-}$ ($K_f = 4.7 \times 10^{13}$). The reaction with silver bromide is:



What mass of $Na_2S_2O_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $Ag(S_2O_3)_2^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $S_2O_3^{2-}$ ion:

- Reaction (1): $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad K_{sp} = 5.0 \times 10^{-13}$
- Reaction (2): $Ag^+(aq) + S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) \quad K_f = 4.7 \times 10^{13}$

In order for 1.00 g of AgBr to dissolve, the $[Ag^+]$ in the solution that results must be low enough for *Q* for Reaction (1) to be smaller than K_{sp} for this reaction. We reduce $[Ag^+]$ by adding $S_2O_3^{2-}$ and thus cause Reaction (2) to shift to the right. We need the following steps to determine what mass of $Na_2S_2O_3$ is needed to provide the necessary $S_2O_3^{2-}$.

1. *We calculate the $[Br^-]$ produced by the complete dissolution of 1.00 g of AgBr (5.33×10^{-3} mol AgBr) in 1.00 L of solution:*

$$[Br^-] = 5.33 \times 10^{-3}\ M$$

- *We use $[Br^-]$ and K_{sp} to determine the maximum possible concentration of Ag^+ that can be present without causing reprecipitation of AgBr:*

$$[Ag^+] = 9.4 \times 10^{-11}\ M$$

- *We determine the $[S_2O_3^{2-}]$ required to make $[Ag^+] = 9.4 \times 10^{-11}$ M after the remaining Ag^+ ion has reacted with $S_2O_3^{2-}$ according to the equation:*

$$Ag^+ + 2\,S_2O_3^{2-} \rightleftharpoons Ag(S_2O_3)_2^{3-} \quad K_f = 4.7 \times 10^{13}$$

Because 5.33×10^{-3} mol of AgBr dissolves:

\[(5.33×10^{−3})−(9.4×10^{−11})=5.33×10^{−3}\ce{\:mol\:Ag(S2O3)2^3-}\ \nonumber]

Thus, at equilibrium: $[Ag(S_2O_3)_2^{3-}]$ = 5.33 × 10^{-3} *M*, [Ag^+] = 9.4× 10^{-11} *M*, and *Q* = K_f = 4.7 × 10^{13}:

$$K_f = \frac{[Ag(S2O3)2^3-]}{[Ag+][S2O3^2-]^2} = 4.7 \times 10^{13}$$

$$[S_2O_3^{2-}] = 1.1 \times 10^{-3}\ M$$

When $[S_2O_3^{2-}]$ is 1.1 × 10^{-3} *M*, [Ag^+] is 9.4 × 10^{-11} *M* and all AgBr remains dissolved.

- *We determine the total number of moles of $S_2O_3^{2-}$ that must be added to the solution.* This equals the amount that reacts with Ag^+ to form $Ag(S_2O_3)_2^{3-}$ plus the amount of free $S_2O_3^{2-}$ in solution at equilibrium. To form 5.33 × 10^{-3} mol of $Ag(S_2O_3)_2^{3-}$ requires 2 × (5.33 × 10^{-3}) mol of $S_2O_3^{2-}$. In addition, 1.1 × 10^{-3} mol of unreacted $S_2O_3^{2-}$ is present (Step 3). Thus, the total amount of $S_2O_3^{2-}$ that must be added is:

$$2 \times (5.33 \times 10^{-3}\text{mol } S_2O_3^{2-}) + 1.1 \times 10^{-3}\text{ mol } S_2O_3^{2-} = 1.18 \times 10^{-2}\text{ mol } S_2O_3^{2-}$$

- *We determine the mass of $Na_2S_2O_3$ required to give 1.18 × 10^{-2} mol $S_2O_3^{2-}$ using the molar mass of $Na_2S_2O_3$:*

$$1.18 \times 10^{-2}\text{ mol } S_2O_3^{2-} \times \frac{158.1\text{ g } Na_2S_2O_3}{1\text{ mol } Na_2S_2O_3} = 1.9\text{ g } Na_2S_2O_3$$

Thus, 1.00 L of a solution prepared from 1.9 g $Na_2S_2O_3$ dissolves 1.0 g of AgBr.

? Exercise 4.3.2

AgCl(*s*), silver chloride, is well known to have a very low solubility: $Ag(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$, K_{sp} = 1.6 × 10^{-10}. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$, K_f = 1.7 × 10^7. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $Ag(NH_3)_2^+$?

Answer

1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

Dissolution versus Weak Electrolyte Formation

We can determine how to shift the concentration of ions in the equilibrium between a slightly soluble solid and a solution of its ions by applying Le Chatelier's principle. For example, one way to control the concentration of manganese(II) ion, Mn^{2+}, in a solution is to adjust the pH of the solution and, consequently, to manipulate the equilibrium between the slightly soluble solid manganese(II) hydroxide, manganese(II) ion, and hydroxide ion:

$$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2\,OH^-(aq) \quad K_{sp} = [Mn^{2+}][OH^-]^2$$

This could be important to a laundry because clothing washed in water that has a manganese concentration exceeding 0.1 mg per liter may be stained by the manganese. We can reduce the concentration of manganese by increasing the concentration of hydroxide ion. We could add, for example, a small amount of NaOH or some other base such as the silicates found in many laundry detergents. As the concentration of OH^- ion increases, the equilibrium responds by shifting to the left and reducing the concentration of Mn^{2+} ion while increasing the amount of solid $Mn(OH)_2$ in the equilibrium mixture, as predicted by Le Chatelier's principle.

✓ Example 4.3.3: Solubility Equilibrium of a Slightly Soluble Solid

What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ in water at equilibrium?

a. $MgCl_2$
b. KOH
c. an acid

d. $NaNO_3$
e. $Mg(OH)_2$

Solution

The equilibrium among solid $Mg(OH)_2$ and a solution of Mg^{2+} and OH^- is:

$$\mathbf{Mg(OH)_2}(s) \rightleftharpoons \mathbf{Mg^{2+}}(aq) + 2\,\mathbf{OH^-}(aq)$$

(a) The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Chatelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{sp}$), and $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.

(b) The reaction shifts to the left to relieve the stress of the additional OH^- ion. $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is greater and $[Mg^{2+}]$ is less than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.

(c) The concentration of OH^- is reduced as the OH^- reacts with the acid. The reaction shifts to the right to relieve the stress of less OH^- ion. In quantitative terms, the decrease in the OH^- concentration causes the reaction quotient to be smaller than the solubility product ($Q < K_{sp}$), and additional $Mg(OH)_2$ dissolves until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More $Mg(OH)_2$ is dissolved.

(d) $NaNO_3$ contains none of the species involved in the equilibrium, so we should expect that it has no appreciable effect on the concentrations of Mg^{2+} and OH^-. (As we have seen previously, dissolved salts change the activities of the ions of an electrolyte. However, the salt effect is generally small, and we shall neglect the slight errors that may result from it.)

(e) The addition of solid $Mg(OH)_2$ has no effect on the solubility of $Mg(OH)_2$ or on the concentration of Mg^{2+} and OH^-. The concentration of $Mg(OH)_2$ does not appear in the equation for the reaction quotient:

$$Q = [\mathbf{Mg^{2+}}][\mathbf{OH^-}]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q, and no shift is required to restore Q to the value of the equilibrium constant.

? Exercise 4.3.3

What is the effect on the amount of solid $NiCO_3$ that dissolves and the concentrations of Ni^{2+} and $\mathbf{CO_3^{2-}}$ when each of the following are added to a mixture of the slightly soluble solid $NiCO_3$ and water at equilibrium?

a. $Ni(NO_3)_2$
b. $KClO_4$
c. $NiCO_3$
d. K_2CO_3
e. HNO_3 (reacts with carbonate giving $\mathbf{HCO_3^-}$ or H_2O and CO_2)

Answer

(a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases, $[\mathbf{CO_3^{2-}}]$ decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid $NiCO_3$; (d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases, $[\mathbf{CO_3^{2-}}]$ increases; (e) mass of $NiCO_3(s)$ decreases, $[Ni^{2+}]$ increases, $[\mathbf{CO_3^{2-}}]$ decreases

Summary

Several systems we encounter consist of multiple equilibria, systems where two or more equilibria processes are occurring simultaneously. Some common examples include acid rain, fluoridation, and dissolution of carbon dioxide in sea water. When looking at these systems, we need to consider each equilibrium separately and then combine the individual equilibrium constants into one solubility product or reaction quotient expression using the tools from the first equilibrium chapter. Le Chatelier's

principle also must be considered, as each reaction in a multiple equilibria system will shift toward reactants or products based on what is added to the initial reaction and how it affects each subsequent equilibrium reaction.

Glossary

multiple equilibrium

system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

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4.E: Equilibria of Other Reaction Classes (Exercises)

15.1: Precipitation and Dissolution

Q15.1.1

Complete the changes in concentrations for each of the following reactions:

$$\underset{x}{\mathrm{AgI}(s)} \longrightarrow \mathrm{Ag^+}(aq) + \underset{\_\_\_\_}{\mathrm{I^-}(aq)} \tag{4.E.1}$$
(4.E.2)

$$\underset{\_\_\_\_}{\mathrm{CaCO_3}(s)} \longrightarrow \mathrm{Ca^{2+}}(aq) + \underset{x}{\mathrm{CO_3^{2-}}(aq)} \tag{4.E.3}$$
(4.E.4)

$$\underset{x}{\mathrm{Mg(OH)_2}(s)} \longrightarrow \mathrm{Mg^{2+}}(aq) + \underset{\_\_\_\_}{2\,\mathrm{OH^-}(aq)} \tag{4.E.5}$$
(4.E.6)

$$\mathrm{Mg_3(PO_4)_2}(s) \longrightarrow 3\,\mathrm{Mg^{2+}}(aq) + \underset{x\_\_\_\_}{2\,\mathrm{PO_4^{3-}}(aq)} \tag{4.E.7}$$
(4.E.8)

$$\mathrm{Ca_5(PO_4)_3OH}(s) \longrightarrow \underset{\_\_\_\_}{5\,\mathrm{Ca^{2+}}(aq)} + \underset{\_\_\_\_}{3\,\mathrm{PO_4^{3-}}(aq)} + \underset{x}{\mathrm{OH^-}(aq)} \tag{4.E.9}$$
(4.E.10)

S15.1.1

$$\underset{x}{\mathrm{AgI}(s)} \longrightarrow \mathrm{Ag^+}(aq) + \underset{\underline{x}}{\mathrm{I^-}(aq)} \tag{4.E.11}$$
(4.E.12)

$$\underset{\underline{x}}{\mathrm{CaCO_3}(s)} \longrightarrow \mathrm{Ca^{2+}}(aq) + \underset{x}{\mathrm{CO_3^{2-}}(aq)} \tag{4.E.13}$$
(4.E.14)

$$\underset{x}{\mathrm{Mg(OH)_2}(s)} \longrightarrow \mathrm{Mg^{2+}}(aq) + \underset{\underline{2x}}{2\,\mathrm{OH^-}(aq)} \tag{4.E.15}$$
(4.E.16)

$$\underset{\underline{3x}}{\mathrm{Mg_3(PO_4)_2}(s)} \longrightarrow 3\,\mathrm{Mg^{2+}}(aq) + \underset{2x}{2\,\mathrm{PO_4^{3-}}(aq)} \tag{4.E.17}$$
(4.E.18)

$$\underset{\underline{5x}}{\mathrm{Ca_5(PO_4)_3OH}(s)} \longrightarrow 5\,\mathrm{Ca^{2+}}(aq) + \underset{\underline{3x}}{3\,\mathrm{PO_4^{3-}}(aq)} + \underset{x}{\mathrm{OH^-}(aq)} \tag{4.E.19}$$
(4.E.20)

Q15.1.2

Complete the changes in concentrations for each of the following reactions:

$$\underset{x}{\mathrm{BaSO_4}(s)} \longrightarrow \mathrm{Ba^{2+}}(aq) + \underset{\_\_\_\_}{\mathrm{SO_4^{2-}}(aq)} \tag{4.E.21}$$
(4.E.22)

$$\underset{\_\_\_\_}{\mathrm{Ag_2SO_4}(s)} \longrightarrow 2\,\mathrm{Ag^+}(aq) + \underset{x}{\mathrm{SO_4^{2-}}(aq)} \tag{4.E.23}$$
(4.E.24)

$$\underset{x}{\mathrm{Al(OH)_3}(s)} \longrightarrow \mathrm{Al^{3+}}(aq) + \underset{\_\_\_\_}{3\,\mathrm{OH^-}(aq)} \tag{4.E.25}$$
(4.E.26)

$$\underset{\_\_\_\_}{\mathrm{Pb(OH)Cl}(s)} \longrightarrow \mathrm{Pb^{2+}}(aq) + \underset{x}{\mathrm{OH^-}(aq)} + \underset{\_\_\_\_}{\mathrm{Cl^-}(aq)} \tag{4.E.27}$$
(4.E.28)

$$\underset{3x}{\mathrm{Ca_3(AsO_4)_2}(s)} \longrightarrow 3\,\mathrm{Ca^{2+}}(aq) + \underset{\_\_\_\_}{2\,\mathrm{AsO_4^{3-}}(aq)} \tag{4.E.29}$$
(4.E.30)

Q15.1.3

How do the concentrations of Ag^+ and CrO_4^{2-} in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

S15.1.3

There is no change. A solid has an activity of 1 whether there is a little or a lot.

Q15.1.4

How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS?

Q15.1.5

What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

S15.1.5

The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

Q15.1.6

Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?

Q15.1.7

Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, ZnS, PbS?

S15.1.7

CaF_2, $MnCO_3$, and ZnS

Q15.1.8

Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

a. $PbCl_2$
b. Ag_2S
c. $Sr_3(PO_4)_2$
d. $SrSO_4$

Q15.1.9

Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

a. LaF_3
b. $CaCO_3$
c. Ag_2SO_4
d. $Pb(OH)_2$

Q15.1.10

a. $\mathrm{LaF_3}(s) \rightleftharpoons \mathrm{La^{3+}}(aq) + 3\,\mathrm{F^-}(aq) \quad K_{sp} = [\mathrm{La^{3+}}][\mathrm{F^-}]^3$;
b. $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]$;
c. $\mathrm{Ag_2SO_4}(s) \rightleftharpoons 2\,\mathrm{Ag^+}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_{sp} = [\mathrm{Ag^+}]^2[\mathrm{SO_4^{2-}}]$;
d. $\mathrm{Pb(OH)_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \quad K_{sp} = [\mathrm{Pb^{2+}}][\mathrm{OH^-}]^2$

Q15.1.11

The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

a. $BaSiF_6$, 0.026 g/100 mL (contains $\mathrm{SiF_6^{2-}}$ ions)
b. $Ce(IO_3)_4$, 1.5×10^{-2} g/100 mL
c. $Gd_2(SO_4)_3$, 3.98 g/100 mL
d. $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains $\mathrm{PtBr_6^{2-}}$ ions)

Q15.1.12

The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

a. $BaSeO_4$, 0.0118 g/100 mL
b. $Ba(BrO_3)_2 \cdot H_2O$, 0.30 g/100 mL
c. $NH_4MgAsO_4 \cdot 6H_2O$, 0.038 g/100 mL
d. $La_2(MoO_4)_3$, 0.00179 g/100 mL

S15.1.12

(a)1.77×10^{-7}; 1.6×10^{-6}; 2.2×10^{-9}; 7.91×10^{-22}

Q15.1.13

Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.

Q15.1.14

Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

a. $KHC_4H_4O_6$
b. PbI_2
c. $Ag_4[Fe(CN)_6]$, a salt containing the $\mathbf{Fe(CN)_4^-}$ ion
d. Hg_2I_2

S15.1.15

2×10^{-2} *M*; 1.3×10^{-3} *M*; 2.27×10^{-9} *M*; 2.2×10^{-10} *M*

Q15.1.16

Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

a. Ag_2SO_4
b. $PbBr_2$
c. AgI
d. $CaC_2O_4 \cdot H_2O$

Q15.1.X

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

a. AgCl(*s*) in 0.025 *M* NaCl
b. CaF_2(*s*) in 0.00133 *M* KF
c. Ag_2SO_4(*s*) in 0.500 L of a solution containing 19.50 g of K_2SO_4
d. $Zn(OH)_2$(*s*) in a solution buffered at a pH of 11.45

S15.1.X

7.2×10^{-9} *M* = $[Ag^+]$, $[Cl^-]$ = 0.025 *M*

Check: $\frac{\mathbf{7.2 \times 10^{-9}\ \mathit{M}}}{\mathbf{0.025\ \mathit{M}}} \times \mathbf{100\%} = \mathbf{2.9 \times 10^{-5}\%}$, an insignificant change;

2.2×10^{-5} *M* = $[Ca^{2+}]$, $[F^-]$ = 0.0013 *M*

Check: $\frac{2.25 \times 10^{-5}\ M}{0.00133\ M} \times 100\% = 1.69\%$. This value is less than 5% and can be ignored.

0.2238 M = $[SO_4^{2-}]$; $[Ag^+] = 2.30 \times 10^{-9}\ M$

Check: $\frac{1.15 \times 10^{-9}}{0.2238} \times 100\% = 5.14 \times 10^{-7}$; the condition is satisfied.

$[OH^-] = 2.8 \times 10^{-3}\ M$; $5.7 \times 10^{-12}\ M = [Zn^{2+}]$

Check: $\frac{5.7 \times 10^{-12}}{2.8 \times 10^{-3}} \times 100\% = 2.0 \times 10^{-7}\%$; x is less than 5% of $[OH^-]$ and is, therefore, negligible.

Q15.1.X

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

a. TlCl(s) in 1.250 M HCl
b. PbI_2(s) in 0.0355 M CaI_2
c. Ag_2CrO_4(s) in 0.225 L of a solution containing 0.856 g of K_2CrO_4
d. $Cd(OH)_2$(s) in a solution buffered at a pH of 10.995

Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

a. TlCl(s) in 0.025 M $TlNO_3$
b. BaF_2(s) in 0.0313 M KF
c. MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$
d. $Ca(OH)_2$(s) in an unbuffered solution initially with a pH of 12.700

S15.1.X

- $[Cl^-] = 7.6 \times 10^{-3}\ M$

Check: $\frac{7.6 \times 10^{-3}}{0.025} \times 100\% = 30\%$

This value is too large to drop x. Therefore solve by using the quadratic equation:

- $[Ti^+] = 3.1 \times 10^{-2}\ M$
- $[Cl^-] = 6.1 \times 10^{-3}$
- $[Ba^{2+}] = 1.7 \times 10^{-3}\ M$

Check: $\frac{1.7 \times 10^{-3}}{0.0313} \times 100\% = 5.5\%$

This value is too large to drop x, and the entire equation must be solved.

- $[Ba^{2+}] = 1.6 \times 10^{-3}\ M$
- $[F^-] = 0.0329\ M$;
- $Mg(NO_3)_2 = 0.02444\ M$

$[C_2O_4^{2-}] = 3.5 \times 10^{-3}$

Check: $\frac{3.5 \times 10^{-3}}{0.02444} \times 100\% = 14\%$

This value is greater than 5%, so the quadratic equation must be used:

- $[C_2O_4^{2-}] = 3.5 \times 10^{-3}\ M$
- $[Mg^{2+}] = 0.0275\ M$
- $[OH^-] = 0.0501\ M$
- $[Ca^{2+}] = 3.15 \times 10^{-3}$

Check: $\frac{3.15 \times 10^{-3}}{0.050} \times 100\% = 6.28\%$

This value is greater than 5%, so a more exact method, such as successive approximations, must be used.

- $[Ca^{2+}] = 2.8 \times 10^{-3}\ M$
- $[OH^-] = 0.053 \times 10^{-2}\ M$

Q15.1.X

Explain why the changes in concentrations of the common ions in Exercise can be neglected.

Q15.1.X

Explain why the changes in concentrations of the common ions in Exercise cannot be neglected.

S15.1.X

The changes in concentration are greater than 5% and thus exceed the maximum value for disregarding the change.

Q15.1.X

Calculate the solubility of aluminum hydroxide, $Al(OH)_3$, in a solution buffered at pH 11.00.

Q15.1.X

Refer to Appendix J for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

S15.1.X

$CaSO_4 \cdot 2H_2O$ is the most soluble Ca salt in mol/L, and it is also the most soluble Ca salt in g/L.

Q15.1.X

Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract. This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.

Q15.1.X

Public Health Service standards for drinking water set a maximum of 250 mg/L ($2.60 \times 10^{-3}\ M$) of SO_4^{2-} because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ ("gyp" water) as a result or passing through soil containing gypsum, $CaSO_4 \cdot 2H_2O$, meet these standards? What is SO_4^{2-} in such water?

S15.1.X

$4.9 \times 10^{-3}\ M = [SO_4^{2-}] = [Ca^{2+}]$; Since this concentration is higher than $2.60 \times 10^{-3}\ M$, "gyp" water does not meet the standards.

Q15.1.X

Perform the following calculations:

a. Calculate $[Ag^+]$ in a saturated aqueous solution of AgBr.
b. What will $[Ag^+]$ be when enough KBr has been added to make $[Br^-] = 0.050\ M$?
c. What will $[Br^-]$ be when enough $AgNO_3$ has been added to make $[Ag^+] = 0.020\ M$?

The solubility product of $CaSO_4 \cdot 2H_2O$ is 2.4×10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 M SO_4^{2-}?

S15.1.X

Mass ($CaSO_4 \cdot 2H_2O$) = 0.34 g/L

Q15.1.X

Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Table E3 for solubility products).

a. TlCl
b. BaF_2
c. Ag_2CrO_4
d. $CaC_2O_4 \cdot H_2O$
e. the mineral anglesite, $PbSO_4$

Q15.1.X

Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Table E3 for solubility products).

a. AgI
b. Ag_2SO_4
c. $Mn(OH)_2$
d. $Sr(OH)_2 \cdot 8H_2O$
e. the mineral brucite, $Mg(OH)_2$

S15.1.X

$[Ag^+] = [I^-] = 1.2 \times 10^{-8}\ M$; $[Ag^+] = 2.86 \times 10^{-2}\ M$, $[SO_4^{2-}] = 1.43 \times 10^{-2}\ M$; $[Mn^{2+}] = 2.2 \times 10^{-5}\ M$, $[OH^-] = 4.5 \times 10^{-5}\ M$; $[Sr^{2+}] = 4.3 \times 10^{-2}\ M$, $[OH^-] = 8.6 \times 10^{-2}\ M$; $[Mg^{2+}] = 1.6 \times 10^{-4}\ M$, $[OH^-] = 3.1 \times 10^{-4}\ M$.

Q15.1.X

The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

a. AgBr: $[Ag^+] = 5.7 \times 10^{-7}\ M$, $[Br^-] = 5.7 \times 10^{-7}\ M$
b. $CaCO_3$: $[Ca^{2+}] = 5.3 \times 10^{-3}\ M$, $[CO_3^{2-}] = 9.0 \times 10^{-7}\ M$
c. PbF_2: $[Pb^{2+}] = 2.1 \times 10^{-3}\ M$, $[F^-] = 4.2 \times 10^{-3}\ M$
d. Ag_2CrO_4: $[Ag^+] = 5.3 \times 10^{-5}\ M$, $3.2 \times 10^{-3}\ M$
e. InF_3: $[In^{3+}] = 2.3 \times 10^{-3}\ M$, $[F^-] = 7.0 \times 10^{-3}\ M$

Q15.1.X

The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

a. TlCl: $[Tl^+] = 1.21 \times 10^{-2}\ M$, $[Cl^-] = 1.2 \times 10^{-2}\ M$
b. $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8 \times 10^{-4}\ M$, $[IO_3^-] = 2.6 \times 10^{-13}\ M$
c. $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132\ M$, $[SO_4^{2-}] = 0.198\ M$
d. Ag_2SO_4: $[Ag^+] = 2.40 \times 10^{-2}\ M$, $[SO_4^{2-}] = 2.05 \times 10^{-2}\ M$
e. $BaSO_4$: $[Ba^{2+}] = 0.500\ M$, $[SO_4^{2-}] = 2.16 \times 10^{-10}\ M$

S15.1.X

2.0×10^{-4}; 5.1×10^{-17}; 1.35×10^{-4}; 1.18×10^{-5}; 1.08×10^{-10}

Q15.1.X

Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Table E3 for K_{sp} values.)

a. $KClO_4$: $[K^+] = 0.01\ M$, $[ClO_4^-] = 0.01\ M$
b. K_2PtCl_6: $[K^+] = 0.01\ M$, $[PtCl_6^{2-}] = 0.01\ M$
c. PbI_2: $[Pb^{2+}] = 0.003\ M$, $[I^-] = 1.3 \times 10^{-3}\ M$
d. Ag_2S: $[Ag^+] = 1 \times 10^{-10}\ M$, $[S^{2-}] = 1 \times 10^{-13}\ M$

Q15.1.X

Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Table E3 for K_{sp} values.)

a. $CaCO_3$: $[Ca^{2+}] = 0.003\ M$, $[\mathbf{CO_3^{2-}}] = 0.003\ M$
b. $Co(OH)_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1 \times 10^{-7}\ M$
c. $CaHPO_4$: $[Ca^{2+}] = 0.01\ M$, $[\mathbf{HPO_4^{2-}}] = 2 \times 10^{-6}\ M$
d. $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01\ M$, $[\mathbf{PO_4^{3-}}] = 1 \times 10^{-13}\ M$

S15.1.X

a. $CaCO_3$ does precipitate.
b. The compound does not precipitate.
c. The compound does not precipitate.
d. The compound precipitates.

Q15.1.X

Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^-.

Q15.1.X

Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 M in Ba^{2+}.

S15.1.X

$1.42 \times 10^{-9}\ M$

Q15.1.X

Calculate the concentration of Sr^{2+} when SrF_2 starts to precipitate from a solution that is 0.0025 M in F^-.

Q15.1.X

Calculate the concentration of $\mathbf{PO_4^{3-}}$ when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+.

S15.1.X

$9.2 \times 10^{-13}\ M$

Q15.1.X

Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 M in Ca^{2+}.

Q15.1.X

Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is $2.50 \times 10^{-6}\ M$ in $\mathbf{CO_3^{2-}}$.

S15.1.X

$[Ag^+] = 1.8 \times 10^{-3}\ M$

Q15.1.X

What $[Ag^+]$ is required to reduce $[\mathbf{CO_3^{2-}}]$ to $8.2 \times 10^{-4}\ M$ by precipitation of Ag_2CO_3?

Q15.1.X

What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0 \times 10^{-4}\ M$ by precipitation of CaF_2?

S15.1.X

6.2×10^{-4}

Q15.1.X

A volume of 0.800 L of a 2×10^{-4}-*M* $Ba(NO_3)_2$ solution is added to 0.200 L of 5×10^{-4} *M* Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.

Q15.1.X

Perform these calculations for nickel(II) carbonate.

a. With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36 \times 10^{-7}$).
b. If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

S15.1.X

2.28 L; 7.3×10^{-7} g

Q15.1.X

Iron concentrations greater than 5.4×10^{-6} *M* in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?

Q15.1.X

A solution is 0.010 *M* in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

S15.1.X

100% of it is dissolved

Q15.1.X

A solution is 0.15 *M* in both Pb^{2+} and Ag^+. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?

Q15.1.X

What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 *M* with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in Appendix J.)

a. $\mathbf{Hg_2^{2+}}$ and Cu^{2+}
b. $\mathbf{SO_4^{2-}}$ and Cl^-
c. Hg^{2+} and Co^{2+}
d. Zn^{2+} and Sr^{2+}
e. Ba^{2+} and Mg^{2+}
f. $\mathbf{CO_3^{2-}}$ and OH^-

S15.1.X

a. $\mathbf{Hg_2^{2+}}$ and Cu^{2+}: Add $\mathbf{SO_4^{2-}}$.
b. $\mathbf{SO_4^{2-}}$ and Cl^-: Add Ba^{2+}.
c. Hg^{2+} and Co^{2+}: Add S^{2-}.
d. Zn^{2+} an Sr^{2+}: Add OH^- until $[OH^-] = 0.050$ *M*.
e. Ba^{2+} and Mg^{2+}: Add $\mathbf{SO_4^{2-}}$.
f. $\mathbf{CO_3^{2-}}$ and OH^-: Add Ba^{2+}.

Q15.1.X

A solution contains 1.0×10^{-5} mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

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Q15.1.X

A solution contains 1.0×10^{-2} mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

S15.1.X

AgI will precipitate first.

Q15.1.X

The calcium ions in human blood serum are necessary for coagulation. Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4 \cdot H_2O$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)

Q15.1.X

About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

S15.1.X

$4 \times 10^{-9}\ M$

Q15.1.X

The pH of normal urine is 6.30, and the total phosphate concentration ($[PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$) is 0.020 *M*. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation? (See Exercise for additional information.)

Q15.1.X

Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

$$Mg^{2+}(aq) + Ca(OH)_2(aq) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

$$Mg(OH)_2(s) + 2\,HCl(aq) \longrightarrow MgCl_2(s) + 2\,H_2O(l)$$

$$MgCl_2(l) \xrightarrow{\text{electrolysis}} Mg(s) + Cl_2(g)$$

Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00×10^3 L of sea water?

S15.1.X

3.99 kg

Q15.1.X

Hydrogen sulfide is bubbled into a solution that is 0.10 *M* in both Pb^{2+} and Fe^{2+} and 0.30 *M* in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[H_2S] = 0.10\ M$). What concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

$$H_2S(aq) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq) \quad K = 1.0 \times 10^{-26}$$

(Hint: The $[H_3O^+]$ changes as metal sulfides precipitate.)

Q15.1.X

Perform the following calculations involving concentrations of iodate ions:

a. The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1×10^{-3} mol/L. Find the K_{sp}.

b. Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ ($K_{sp} = 7.4 \times 10^{-8}$).

S15.1.X

3.1×10^{-11}; $[Cu^{2+}] = 2.6 \times 10^{-3}$; $[IO_3^-] = 5.3 \times 10^{-3}$

Q15.1.X

Calculate the molar solubility of AgBr in 0.035 *M* NaBr ($K_{sp} = 5 \times 10^{-13}$).

Q15.1.X

How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-*M* $PbCl_2$ solution ($K_{sp} = 1.2 \times 10^{-15}$)?

S15.1.X

1.8×10^{-5} g $Pb(OH)_2$

Q15.1.X

Use the simulation from the earlier Link to Learning to complete the following exercise:. Using 0.01 g CaF_2, give the K_{sp} values found in a 0.2-*M* solution of each of the salts. Discuss why the values change as you change soluble salts.

Q15.1.X

How many grams of Milk of Magnesia, $Mg(OH)_2$ (s) (58.3 g/mol), would be soluble in 200 mL of water. $K_{sp} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)

S15.1.X

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2\,OH^- \tag{4.E.31}$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 \tag{4.E.32}$$

\[1.14×10^{-3} g $Mg(OH)_2$\]

Q15.1.X

Two hypothetical salts, LM_2 and LQ, have the same molar solubility in H_2O. If K_{sp} for LM_2 is 3.20×10^{-5}, what is the K_{sp} value for LQ?

Q15.1.X

Which of the following carbonates will form first? Which of the following will form last? Explain.

a. $MgCO_3$ $K_{sp} = 3.5 \times 10^{-8}$
b. $CaCO_3$ $K_{sp} = 4.2 \times 10^{-7}$
c. $SrCO_3$ $K_{sp} = 3.9 \times 10^{-9}$
d. $BaCO_3$ $K_{sp} = 4.4 \times 10^{-5}$
e. $MnCO_3$ $K_{sp} = 5.1 \times 10^{-9}$

S15.1.X

$SrCO_3$ will form first, since it has the smallest K_{sp} value it is the least soluble. $BaCO_3$ will be the last to precipitate, it has the largest K_{sp} value.

Q15.1.X

How many grams of $Zn(CN)_2$(s) (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2$(s) is 3.0×10^{-16}.

15.2: Lewis Acids and Bases

Q15.2.X

Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?

S15.2.X

when the amount of solid is so small that a saturated solution is not produced

Q15.2.X

Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.

Q15.2.X

Calculate the cadmium ion concentration, $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 *M* $Cd(NO_3)_2$ with 1.150 L of 0.100 $NH_3(aq)$.

S15.2.X

2.35×10^{-4} *M*

Q15.2.X

Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.

S15.2.X

Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion $\mathbf{AlF_6^{3-}}$ the dissociation reaction is:

$$\mathbf{AlF_6^{3-} \rightleftharpoons Al^{3+} + 6\,F^-} \quad and \quad K_d = \frac{[Al^{3+}][F^-]^6}{[AlF_6^{3-}]} = 2 \times 10^{-24} \tag{4.E.33}$$

Q15.2.X

Calculate the value of the formation constant, K_f, for $\mathbf{AlF_6^{3-}}$.

S15.2.X

5×10^{23}

Q15.2.X

Using the value of the formation constant for the complex ion $\mathbf{Co(NH_3)_6^{2+}}$, calculate the dissociation constant.

Q15.2.X

Using the dissociation constant, $K_d = 7.8 \times 10^{-18}$, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-*M* solution of $\mathbf{Cd(CN)_4^{2-}}$.

S15.2.X

This table has two main columns and three rows. The first row for the first column does not have a heading and then has the following in the first column: Initial concentration (M) and Equilibrium (M). The second column has the header, “[C d (C N) subscript 4 to the second power superscript negative sign] [C N superscript negative sign] [C d to the second power superscript positive sign].” Under the second column is a subgroup of two rows and three columns. The first column contains the following: 0.250 and 0.250 minus x. The second column contains the following: 0 and 4 x. The third column contains the following: 0 and x.

$[Cd^{2+}] = 9.5 \times 10^{-5}$ *M*; $[CN^-] = 3.8 \times 10^{-4}$ *M*

Q15.2.X

Using the dissociation constant, $K_d = 3.4 \times 10^{-15}$, calculate the equilibrium concentrations of Zn^{2+} and OH^- in a 0.0465-*M* solution of $\mathbf{Zn(OH)_4^{2-}}$.

Q15.2.X

Using the dissociation constant, $K_d = 2.2 \times 10^{-34}$, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-*M* solution of $\mathbf{Co(NH_3)_6^{3+}}$.

S15.2.X

$[Co^{3+}] = 3.0 \times 10^{-6}\ M$; $[NH_3] = 1.8 \times 10^{-5}\ M$

Q15.2.X

Using the dissociation constant, $K_d = 1 \times 10^{-44}$, calculate the equilibrium concentrations of Fe^{3+} and CN^- in a 0.333 M solution of $\mathbf{Fe(CN)_6^{3-}}$.

Q15.2.X

Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN.

S15.2.X

1.3 g

Q15.2.X

Calculate the minimum concentration of ammonia needed in 1.0 L of solution to dissolve 3.0×10^{-3} mol of silver bromide.

Q15.2.X

A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $Na_2S_2O_3 \cdot 5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as $\mathbf{Ag(S_2O_3)_2^{3-}}$ ($K_f = 4.7 \times 10^{13}$)?

S15.2.X

0.80 g

Q15.2.X

We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^+) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

Q15.2.X

Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

a. $\mathbf{CO_2 + OH^- \longrightarrow HCO_3^-}$
b. $\mathbf{B(OH)_3 + OH^- \longrightarrow B(OH)_4^-}$
c. $\mathbf{I^- + I_2 \longrightarrow I_3^-}$
d. $\mathbf{AlCl_3 + Cl^- \longrightarrow AlCl_4^-}$ (use Al-Cl single bonds)
e. $\mathbf{O^{2-} + SO_3 \longrightarrow SO_4^{2-}}$

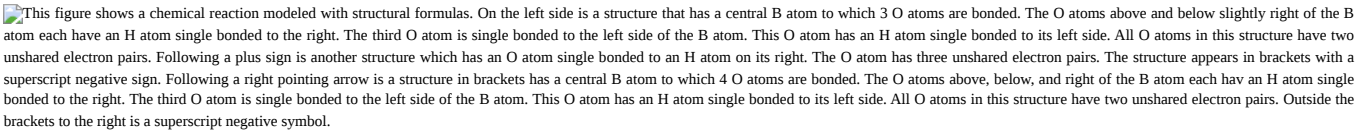
S15.2.X

(a)

This figure shows a chemical reaction modeled with structural formulas. On the left side is a structure with a central C atom. O atoms, each with two unshared electron pairs, are double bonded to the left and right sides of the C atom. Following a plus sign is another structure in brackets which has an O atom with three unshared electron dot pairs single bonded to an H atom on the right. Outside the brackets is superscript negative sign. Following a right pointing arrow is a structure in brackets that has a central C atom to which 3 O atoms are bonded. Above and slightly to the right, one of the O atoms is connected with a double bond. This O atom has two unshared electron pairs. The second O atom is single bonded below and slightly to the right. This O atom has three unshared electron pairs. The third O atom is bonded to the left of the C atom. This O atom has two unshared electron pairs and an H atom single bonded to its left. Outside the brackets to the right is a superscript negative symbol.

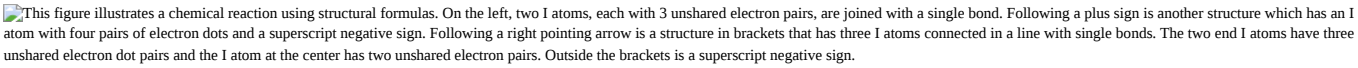
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(b)


This figure shows a chemical reaction modeled with structural formulas. On the left side is a structure that has a central B atom to which 3 O atoms are bonded. The O atoms above and below slightly right of the B atom each have an H atom single bonded to the right. The third O atom is single bonded to the left side of the B atom. This O atom has an H atom single bonded to its left side. All O atoms in this structure have two unshared electron pairs. Following a plus sign is another structure which has an O atom single bonded to an H atom on its right. The O atom has three unshared electron pairs. The structure appears in brackets with a superscript negative sign. Following a right pointing arrow is a structure in brackets has a central B atom to which 4 O atoms are bonded. The O atoms above, below, and right of the B atom each hav an H atom single bonded to the right. The third O atom is single bonded to the left side of the B atom. This O atom has an H atom single bonded to its left side. All O atoms in this structure have two unshared electron pairs. Outside the brackets to the right is a superscript negative symbol.

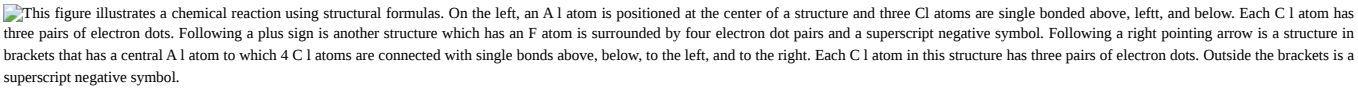
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(c)


This figure illustrates a chemical reaction using structural formulas. On the left, two I atoms, each with 3 unshared electron pairs, are joined with a single bond. Following a plus sign is another structure which has an I atom with four pairs of electron dots and a superscript negative sign. Following a right pointing arrow is a structure in brackets that has three I atoms connected in a line with single bonds. The two end I atoms have three unshared electron dot pairs and the I atom at the center has two unshared electron pairs. Outside the brackets is a superscript negative sign.

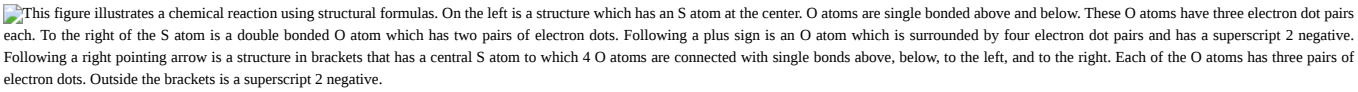
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(d)


This figure illustrates a chemical reaction using structural formulas. On the left, an A l atom is positioned at the center of a structure and three Cl atoms are single bonded above, leftt, and below. Each C l atom has three pairs of electron dots. Following a plus sign is another structure which has an F atom is surrounded by four electron dot pairs and a superscript negative symbol. Following a right pointing arrow is a structure in brackets that has a central A l atom to which 4 C l atoms are connected with single bonds above, below, to the left, and to the right. Each C l atom in this structure has three pairs of electron dots. Outside the brackets is a superscript negative symbol.

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(e)


This figure illustrates a chemical reaction using structural formulas. On the left is a structure which has an S atom at the center. O atoms are single bonded above and below. These O atoms have three electron dot pairs each. To the right of the S atom is a double bonded O atom which has two pairs of electron dots. Following a plus sign is an O atom which is surrounded by four electron dot pairs and has a superscript 2 negative. Following a right pointing arrow is a structure in brackets that has a central S atom to which 4 O atoms are connected with single bonds above, below, to the left, and to the right. Each of the O atoms has three pairs of electron dots. Outside the brackets is a superscript 2 negative.

Q15.2.X

Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

a. $\mathrm{CS_2 + SH^- \longrightarrow HCS_3^-}$
b. $\mathrm{BF_3 + F^- \longrightarrow BF_4^-}$
c. $\mathrm{I^- + SnI_2 \longrightarrow SnI_3^-}$
d. $\mathrm{Al(OH)_3 + OH^- \longrightarrow Al(OH)_4^-}$
e. $\mathrm{F^- + SO_3 \longrightarrow SFO_3^-}$

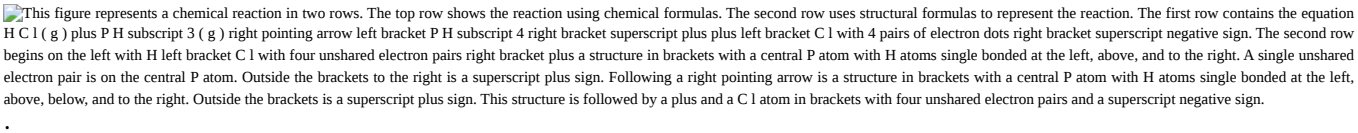
Q15.2.X

Using Lewis structures, write balanced equations for the following reactions:

a. $\mathrm{HCl}(g) + \mathrm{PH_3}(g) \longrightarrow$
b. $\mathrm{H_3O^+ + CH_3^- \longrightarrow}$
c. $\mathrm{CaO + SO_3 \longrightarrow}$
d. $\mathrm{NH_4^+ + C_2H_5O^- \longrightarrow}$

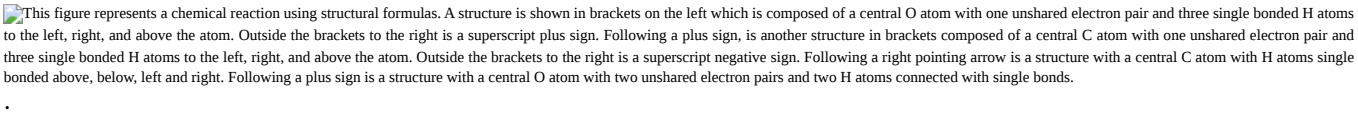
S15.2.X

(a)


This figure represents a chemical reaction in two rows. The top row shows the reaction using chemical formulas. The second row uses structural formulas to represent the reaction. The first row contains the equation H C l (g) plus P H subscript 3 (g) right pointing arrow left bracket P H subscript 4 right bracket superscript plus plus left bracket C l with 4 pairs of electron dots right bracket superscript negative sign. The second row begins on the left with H left bracket C l with four unshared electron pairs right bracket plus a structure in brackets with a central P atom with H atoms single bonded at the left, above, and to the right. A single unshared electron pair is on the central P atom. Outside the brackets to the right is a superscript plus sign. Following a right pointing arrow is a structure in brackets with a central P atom with H atoms single bonded at the left, above, below, and to the right. Outside the brackets is a superscript plus sign. This structure is followed by a plus and a C l atom in brackets with four unshared electron pairs and a superscript negative sign.

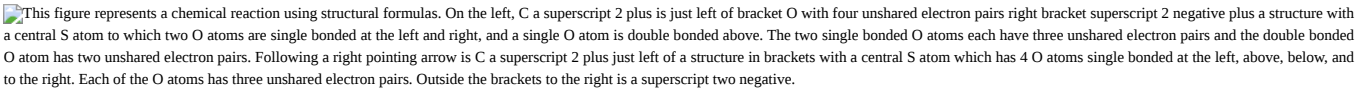
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$\mathrm{H_3O^+ + CH_3^- \longrightarrow CH_4 + H_2O}$


This figure represents a chemical reaction using structural formulas. A structure is shown in brackets on the left which is composed of a central O atom with one unshared electron pair and three single bonded H atoms to the left, right, and above the atom. Outside the brackets to the right is a superscript plus sign. Following a plus sign, is another structure in brackets composed of a central C atom with one unshared electron pair and three single bonded H atoms to the left, right, and above the atom. Outside the brackets to the right is a superscript negative sign. Following a right pointing arrow is a structure with a central C atom with H atoms single bonded above, below, left and right. Following a plus sign is a structure with a central O atom with two unshared electron pairs and two H atoms connected with single bonds.

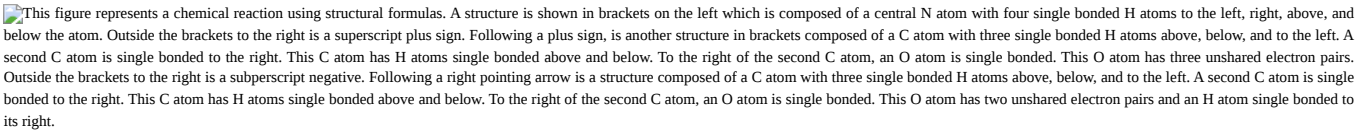
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$$CaO + SO_3 \longrightarrow CaSO_4$$


This figure represents a chemical reaction using structural formulas. On the left, C a superscript 2 plus is just left of bracket O with four unshared electron pairs right bracket superscript 2 negative plus a structure with a central S atom to which two O atoms are single bonded at the left and right, and a single O atom is double bonded above. The two single bonded O atoms each have three unshared electron pairs and the double bonded O atom has two unshared electron pairs. Following a right pointing arrow is C a superscript 2 plus just left of a structure in brackets with a central S atom which has 4 O atoms single bonded at the left, above, below, and to the right. Each of the O atoms has three unshared electron pairs. Outside the brackets to the right is a superscript two negative.

;

$$NH_4^+ + C_2H_5O^- \longrightarrow C_2H_5OH + NH_3$$


This figure represents a chemical reaction using structural formulas. A structure is shown in brackets on the left which is composed of a central N atom with four single bonded H atoms to the left, right, above, and below the atom. Outside the brackets to the right is a superscript plus sign. Following a plus sign, is another structure in brackets composed of a C atom with three single bonded H atoms above, below, and to the left. A second C atom is single bonded to the right. This C atom has H atoms single bonded above and below. To the right of the second C atom, an O atom is single bonded. This O atom has three unshared electron pairs. Outside the brackets to the right is a subperscript negative. Following a right pointing arrow is a structure composed of a C atom with three single bonded H atoms above, below, and to the left. A second C atom is single bonded to the right. This C atom has H atoms single bonded above and below. To the right of the second C atom, an O atom is single bonded. This O atom has two unshared electron pairs and an H atom single bonded to its right.

Q15.2.X

Calculate $[HgCl_4^{2-}]$ in a solution prepared by adding 0.0200 mol of NaCl to 0.250 L of a 0.100-*M* $HgCl_2$ solution.

Q15.2.X

In a titration of cyanide ion, 28.72 mL of 0.0100 *M* $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with CN^- goes to completion, producing the $Ag(CN)_2^-$ complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of $Ag(CN)_2^-$. How many grams of NaCN were in the original sample?

S15.2.X

0.0281 g

Q15.2.X

What are the concentrations of Ag^+, CN^-, and $Ag(CN)_2^-$ in a saturated solution of AgCN?

Q15.2.X

In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

S15.2.X

$$HNO_3(l) + HF(l) \longrightarrow H_2NO_3^+ + F^-;\ HF(l) + BF_3(g) \longrightarrow H^+ + BF_4^-$$

Q15.2.X

The simplest amino acid is glycine, $H_2NCH_2CO_2H$. The common feature of amino acids is that they contain the functional groups: an amine group, $–NH_2$, and a carboxylic acid group, $–CO_2H$. An amino acid can function as either an acid or a base. For glycine, the acid strength of the carboxyl group is about the same as that of acetic acid, CH_3CO_2H, and the base strength of the amino group is slightly greater than that of ammonia, NH_3.

Q15.2.X

Write the Lewis structures of the ions that form when glycine is dissolved in 1 *M* HCl and in 1 *M* KOH.

Q15.2.X

Write the Lewis structure of glycine when this amino acid is dissolved in water. (Hint: Consider the relative base strengths of the $–NH_2$ and $–CO_2–$ groups.)

Q15.2.X

Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

a. Write an equation for its reaction with water.

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b. Predict the shape of the anion thus formed.
c. What is the hybridization on the boron consistent with the shape you have predicted?

S15.2.X

$\mathbf{H_3BO_3 + H_2O \longrightarrow H_4BO_4^- + H^+}$; The electronic and molecular shapes are the same—both tetrahedral. The tetrahedral structure is consistent with sp^3 hybridization.

15.3: Multiple Equilibria

Q15.3.1

A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?

Q15.3.2

Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$.

S15.3.2

0.014 *M*

Q15.3.3

Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of $\mathbf{Zn(CN)_4^{2-}}$.

Q15.3.4

Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3.

S15.3.2

1.0×10^{-13} *M*

Q15.3.5

Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^-.

Q15.3.6

Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 *M* CN^-.

S15.3.2

9×10^{-22} *M*

Q15.3.7

Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.025 *M* NH_3. Assume the volume is 1.00 L.

Q15.3.8

The equilibrium constant for the reaction $\mathbf{Hg^{2+}(\mathit{aq}) + 2\,Cl^-(\mathit{aq}) \rightleftharpoons HgCl_2(\mathit{aq})}$ is 1.6×10^{13}. Is $HgCl_2$ a strong electrolyte or a weak electrolyte? What are the concentrations of Hg^{2+} and Cl^- in a 0.015-*M* solution of $HgCl_2$?

S15.3.2

6.2×10^{-6} *M* = $[Hg^{2+}]$; 1.2×10^{-5} *M* = $[Cl^-]$; The substance is a weak electrolyte because very little of the initial 0.015 *M* $HgCl_2$ dissolved.

Q15.3.9

Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and $\mathbf{NH_4^+}$.

Q15.3.X

Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 *M* NH_3 and 0.400 *M* NH_4^+.

S15.3.2

$[OH^-] = 4.5 \times 10^{-5}$; $[Al^{3+}] = 2.1 \times 10^{-20}$ (molar solubility)

Q15.3.10 Edit section

What is the molar solubility of CaF_2 in a 0.100-*M* solution of HF? K_a for HF = 7.2×10^{-4}.

Q15.3.X

What is the molar solubility of $BaSO_4$ in a 0.250-*M* solution of $NaHSO_4$? K_a for HSO_4^- = 1.2×10^{-2}.

S15.3.2

- $[SO_4^{2-}] = 0.049\ M$
- $[Ba^{2+}] = 2.2 \times 10^{-9}$ (molar solubility)

Q15.3.X

What is the molar solubility of $Tl(OH)_3$ in a 0.10-*M* solution of NH_3?

Q15.3.X

What is the molar solubility of $Pb(OH)_2$ in a 0.138-*M* solution of CH_3NH_2?

S15.3.2

- $[OH^-] = 7.6 \times 10^{-3}\ M$
- $[Pb^{2+}] = 4.8 \times 10^{-12}$ (molar solubility)

Q15.3.X

A solution of 0.075 *M* $CoBr_2$ is saturated with H_2S ($[H_2S] = 0.10\ M$). What is the minimum pH at which CoS begins to precipitate?

$$CoS(s) \rightleftharpoons Co^{2+}(aq) + S^{2-}(aq) \quad K_{sp} = 4.5 \times 10^{-27}$$

$$H_2S(aq) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq) \quad K = 1.0 \times 10^{-26}$$

A 0.125-*M* solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S] = 0.10\ M$). At what pH does MnS begin to precipitate?

$$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq) \quad K_{sp} = 4.3 \times 10^{-22}$$

$$H_2S(aq) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq) \quad K = 1.0 \times 10^{-26}$$

S15.3.2

3.27

Q15.3.X

Calculate the molar solubility of BaF_2 in a buffer solution containing 0.20 *M* HF and 0.20 *M* NaF.

Q15.3.X

Calculate the molar solubility of $CdCO_3$ in a buffer solution containing 0.115 *M* Na_2CO_3 and 0.120 *M* $NaHCO_3$

S15.3.2

- $[CO_3^{2-}] = 0.115\ M$
- $[Cd^{2+}] = 3 \times 10^{-12}\ M$

Q15.3.X

To a 0.10-*M* solution of $Pb(NO_3)_2$ is added enough HF(*g*) to make [HF] = 0.10 *M*.

a. Does PbF_2 precipitate from this solution? Show the calculations that support your conclusion.

b. What is the minimum pH at which PbF_2 precipitates?

Calculate the concentration of Cd^{2+} resulting from the dissolution of $CdCO_3$ in a solution that is 0.010 *M* in H_2CO_3.

S15.3.2

1×10^{-5} *M*

Q15.3.X

Both AgCl and AgI dissolve in NH_3.

a. What mass of AgI dissolves in 1.0 L of 1.0 *M* NH_3?
b. What mass of AgCl dissolves in 1.0 L of 1.0 *M* NH_3?

Calculate the volume of 1.50 *M* CH_3CO_2H required to dissolve a precipitate composed of 350 mg each of $CaCO_3$, $SrCO_3$, and $BaCO_3$.

S15.3.2

0.0102 L (10.2 mL)

Q15.3.X

Even though $Ca(OH)_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $Ca(OH)_2$?

Q15.3.X

What mass of NaCN must be added to 1 L of 0.010 *M* $Mg(NO_3)_2$ in order to produce the first trace of $Mg(OH)_2$?

S15.3.2

5×10^{-3} g

Q15.3.X

Magnesium hydroxide and magnesium citrate function as mild laxatives when they reach the small intestine. Why do magnesium hydroxide and magnesium citrate, two very different substances, have the same effect in your small intestine. (Hint: The contents of the small intestine are basic.)

Q15.3.X

The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:

$$\mathbf{MgF_2}(s) \rightleftharpoons \mathbf{Mg^{2+}}(aq) + \mathbf{2\,F^-}(aq)$$

In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is 1.21×10^{-3} *M*. The equilibrium is represented by the preceding equation.

a. Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.
b. Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
c. Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00×10^{-3}-*M* solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00×10^{-3}-*M* solution of NaF at 18 °C. Show the calculations to support your prediction.
d. At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is 1.17×10^{-3} *M*. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

S15.3.2

$K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$; 7.09×10^{-7} *M*

Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[Mg^{2+}][F^-]^2$ with K_{sp}. If this value is larger than K_{sp}, precipitation will occur. 0.1000 L × 3.00 × 10^{-3} *M* $Mg(NO_3)_2$ = 0.3000 L × *M* $Mg(NO_3)_2$ *M* $Mg(NO_3)_2$ = 1.00 × 10^{-3} *M* 0.2000 L × 2.00 × 10^{-3} *M* NaF = 0.3000 L × *M* NaF *M* NaF = 1.33 × 10^{-3} *M* ion product = (1.00 × 10^{-3})(1.33 × 10^{-3})^2 = 1.77 × 10^{-9} This value is smaller than K_{sp}, so no precipitation will occur. MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Chatelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case. Therefore, the reaction is exothermic.

Q15.3.X

Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.

Q15.3.X

Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_3$, ZnS, PbI_2? Explain your answer.

BaF_2, $Ca_3(PO_4)_2$, ZnS; each is a salt of a weak acid, and the $[H_3O^+]$ from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations

Q15.3.X

What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ and water at equilibrium?

a. $MgCl_2$
b. KOH
c. $HClO_4$
d. $NaNO_3$
e. $Mg(OH)_2$

Q15.3.X

What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and HPO_4^- when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?

a. $CaCl_2$
b. HCl
c. $KClO_4$
d. NaOH
e. $CaHPO_4$

S15.3.X

Effect on amount of solid $CaHPO_4$, $[Ca^{2+}]$, $[OH^-]$: increase, increase, decrease; decrease, increase, decrease; no effect, no effect, no effect; decrease, increase, decrease; increase, no effect, no effect

Q15.3.X

Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the PO_4^{3-} ion is a weak base.)

Q15.3.X

A volume of 50 mL of 1.8 *M* NH_3 is mixed with an equal volume of a solution containing 0.95 g of $MgCl_2$. What mass of NH_4Cl must be added to the resulting solution to prevent the precipitation of $Mg(OH)_2$?

S15.3.X

7.1 g

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CHAPTER OVERVIEW

5: Electrochemistry

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General Chemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

5.1: Balancing Oxidation-Reduction Reactions
5.2: Galvanic Cells
5.3: Standard Reduction Potentials
5.4: The Nernst Equation
5.5: Batteries and Fuel Cells
5.6: Corrosion
5.7: Electrolysis
5.E: Electrochemistry (Exercises)

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5.1: Balancing Oxidation-Reduction Reactions

Learning Objectives

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (Figure **5.1.1**). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric current is the rate of flow of charge.



Figure **5.1.1**: Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay).

The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second (1 A = 1 C/s). An electric current flows in a path, called an electric circuit. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Table **5.1.1** summarizes some of this information about electricity.

Table **5.1.1**: Common Electrical Terms

Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	1.602×10^{-19} C
Electric current	The movement of charge	ampere = A = 1 C/s
Electric potential	The force trying to move the charge	volt = V = J/C
Electric field	The force acting upon other charges in the vicinity	

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The half-reaction method splits oxidation-reduction reactions into their oxidation “half” and reduction “half” to make finding the overall equation easier.

Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Fe^{3+}}(aq)$$

We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+}; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+}.

$$\text{oxidation (unbalanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq)$$
$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)$$

In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.

$$\text{charge not balanced: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:

$$\text{oxidation (balanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}$$

You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

$$\text{Fe: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]\text{? Yes.}$$

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is [(−1) × (1) + (8) × (+1)], or +7, while the total charge on the right side is [(1) × (+2) + (4) × (0)], or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.

$$\text{Reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

You should check this half-reaction for each atom type and for the charge, as well:

$$\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}$$
$$\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]\text{? Yes.}$$

Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+}. In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter,

the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent. We now have two balanced half-reactions.

$$\text{oxidation: } Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-$$
$$\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives

$$\text{oxidation: } 5 \times (Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-)$$
$$\underline{\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)}$$
$$\text{overall: } 5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they "cancel." Carefully check each side of the overall equation to verify everything was combined correctly:

$$\text{Fe: Does } (5 \times 1) = (5 \times 1)\text{? Yes.}$$
$$\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}$$
$$\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [5 \times (+2) + 1 \times (-1) + 8 \times (+1)] = [5 \times (+3) + 1 \times (+2)]\text{? Yes.}$$

Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced overall equation in basic solution is to start with the balanced equation in acidic solution, then "convert" it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:

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

However, under basic conditions, MnO_4^- normally reduces to MnO_2 and iron will be present as either $Fe(OH)_2$ or $Fe(OH)_3$. For these reasons, under basic conditions, this reaction will be

$$3\,Fe(OH)_2(s) + MnO_4^-(aq) + 2\,H_2O(l) \longrightarrow 3\,Fe(OH)_3(s) + MnO_2(s) + OH^-(aq)$$

(Under very basic conditions MnO_4^- will reduce to MnO_4^{2-}, instead of MnO_2.)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. This will work if the acidic and basic reactants and products are the same or if the basic reactants and products are used before the conversion from acidic or basic. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions (H^+) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion (OH^-) to produce water.

Let us now try a basic equation. We will start with the following basic reaction:

$$Cl^-(aq) + MnO_4^-(aq) \longrightarrow ClO_3^-(aq) + MnO_2(s)$$

Balancing this as acid gives

$$Cl^-(aq) + 2\,MnO_4^-(aq) + 2\,H^+(aq) \longrightarrow ClO_3^-(aq) + 2\,MnO_2(s) + H_2O(l)$$

In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:

$$\begin{gathered}\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + (2\,\mathrm{H^+} + 2\,\mathrm{OH^-})(aq) \\ \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{OH^-}(aq)\end{gathered}$$

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + (2\,\mathrm{H_2O})(l) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{OH^-}(aq)$$

Note that both sides of the equation show water. Simplifying should be done when necessary, and gives the desired equation. In this case, it is necessary to remove one H_2O from each side of the reaction arrows.

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + 2\,\mathrm{OH^-}(aq)$$

Again, check each side of the overall equation to make sure there are no errors:

$$\begin{gathered}\text{Cl: Does } (1 \times 1) = (1 \times 1)\text{? Yes.} \\ \text{Mn: Does } (2 \times 1) = (2 \times 1)\text{? Yes.} \\ \text{H: Does } (1 \times 2) = (2 \times 1)\text{? Yes.} \\ \text{O: Does } (2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)\text{? Yes.} \\ \text{Charge: Does } [1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]\text{? Yes.}\end{gathered}$$

Everything checks, so this is the overall equation in basic solution.

Example 5.1.1: Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Cr_2O_7^{2-}}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.

$$\begin{gathered}\text{oxidation (unbalanced): } \mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) \\ \text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)\end{gathered}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } 2\,\mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14 H^+ on the right:

$$\text{oxidation (unbalanced): } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq)$$

The left side of the equation has a total charge of [2 × (+3) = +6], and the right side a total charge of [−2 + 14 × (+1) = +12]. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq) + 6\,\mathrm{e^-}$$

Checking the half-reaction:

$$\begin{gathered}\text{Cr: Does } (2 \times 1) = (1 \times 2)\text{? Yes.} \\ \text{H: Does } (7 \times 2) = (14 \times 1)\text{? Yes.} \\ \text{O: Does } (7 \times 1) = (1 \times 7)\text{? Yes.} \\ \text{Charge: Does } [2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]\text{? Yes.}\end{gathered}$$

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^+ to convert the oxygen into four water molecules:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

Then add five electrons to the left side to balance the charge:

$$\text{reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}\\&\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}\\&\text{Charge: Does } [1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq) + 6\,\mathrm{e^-}\\&\text{reduction: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)\end{aligned}$$

The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:

$$\begin{aligned}&10\,\mathrm{Cr^{3+}}(aq) + 35\,\mathrm{H_2O}(l) + 6\,\mathrm{MnO_4^-}(aq) + 48\,\mathrm{H^+}(aq)\\&\longrightarrow 5\,\mathrm{Cr_2O_7^{2-}}(aq) + 70\,\mathrm{H^+}(aq) + 6\,\mathrm{Mn^{2+}}(aq) + 24\,\mathrm{H_2O}(l)\end{aligned}$$

$$10\,\mathrm{Cr^{3+}}(aq) + 11\,\mathrm{H_2O}(l) + 6\,\mathrm{MnO_4^-}(aq) \longrightarrow 5\,\mathrm{Cr_2O_7^{2-}}(aq) + 22\,\mathrm{H^+}(aq) + 6\,\mathrm{Mn^{2+}}(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (6 \times 1) = (6 \times 1)\text{? Yes.}\\&\text{Cr: Does } (10 \times 1) = (5 \times 2)\text{? Yes.}\\&\text{H: Does } (11 \times 2) = (22 \times 1)\text{? Yes.}\\&\text{O: Does } (11 \times 1 + 6 \times 4) = (5 \times 7)\text{? Yes.}\\&\text{Charge: Does } [10 \times (+3) + 6 \times (-1)] = [5 \times (-2) + 22 \times (+1) + 6 \times (+2)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution.

? Exercise 5.1.1

Balance the following equation in acidic solution:

$$\mathrm{Hg_2^{2+}} + \mathrm{Ag} \longrightarrow \mathrm{Hg} + \mathrm{Ag^+}$$

Answer

$$\mathrm{Hg_2^{2+}}(aq) + 2\,\mathrm{Ag}(s) \longrightarrow 2\,\mathrm{Hg}(l) + 2\,\mathrm{Ag^+}(aq)$$

✔ Example 5.1.2: Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{MnO_2}(s) + \mathrm{CrO_4^{2-}}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction

$$\begin{aligned}&\text{oxidation (unbalanced): } \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq)\\&\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{MnO_2}(s)\end{aligned}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the "left over" hydrogen appears as five H^+ on the right side:

$$\text{oxidation (unbalanced): } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq)$$

The left side of the equation has a total charge of [0], and the right side a total charge of [−2 + 5 × (+1) = +3]. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq) + 3\,e^-$$

Checking the half-reaction:

$$\begin{aligned}&\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (1 \times 3 + 1 \times 2) = (5 \times 1)\text{? Yes.}\\&\text{O: Does } (1 \times 3 + 1 \times 1) = (4 \times 1)\text{? Yes.}\\&\text{Charge: Does } [0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]\text{? Yes.}\end{aligned}$$

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:

$$\text{reduction (unbalanced): } MnO_4^-(aq) + 4\,H^+(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Then add three electrons to the left side to balance the charge:

$$\text{reduction (balanced): } MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (4 \times 1) = (2 \times 2)\text{? Yes.}\\&\text{O: Does } (1 \times 4) = (1 \times 2 + 2 \times 1)\text{? Yes.}\\&\text{Charge: Does } [1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } Cr(OH)_3(s) + H_2O(l) \longrightarrow CrO_4^{2-}(aq) + 5\,H^+(aq) + 3\,e^-\\&\text{reduction: } MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow MnO_2(s) + 2\,H_2O(l)\end{aligned}$$

In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.

$$\begin{aligned}&MnO_4^-(aq) + 4\,H^+(aq) + Cr(OH)_3(s) + H_2O(l)\\&\longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\,H_2O(l) + 5\,H^+(aq)\end{aligned}$$

$$MnO_4^-(aq) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H_2O(l) + H^+(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\&\text{H: Does } (1 \times 3) = (2 \times 1 + 1 \times 1)\text{? Yes.}\\&\text{O: Does } (1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)\text{? Yes.}\\&\text{Charge: Does } [1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:

$$\begin{aligned}&OH^-(aq) + MnO_4^-(aq) + Cr(OH)_3(s)\\&\longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H_2O(l) + (H^+ + OH^-)(aq)\end{aligned}$$

$$OH^-(aq) + MnO_4^-(aq) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\,H_2O(l)$$

Checking each side of the equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.
Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.
H: Does $(1 \times 1 + 1 \times 3) = (2 \times 2)$? Yes.
O: Does $(1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)$? Yes.
Charge: Does $[1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]$? Yes.

This is the balanced equation in basic solution.

? Exercise 5.1.2

Balance the following in the type of solution indicated.

a. $H_2 + Cu^{2+} \longrightarrow Cu$ (acidic solution)
b. $H_2 + Cu(OH)_2 \longrightarrow Cu$ (basic solution)
c. $Fe + Ag^+ \longrightarrow Fe^{2+} + Ag$
d. Identify the oxidizing agents in reactions (a), (b), and (c).
e. Identify the reducing agents in reactions (a), (b), and (c).

Answer a

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^+(aq) + Cu(s)$$

Answer b

$$H_2(g) + Cu(OH)_2(s) \longrightarrow 2\,H_2O(l) + Cu(s)$$

Answer c

$$Fe(s) + 2\,Ag^+(aq) \longrightarrow Fe^{2+}(aq) + 2\,Ag(s)$$

Answer d

oxidizing agent = species reduced: Cu^{2+}, $Cu(OH)_2$, Ag^+

Answer e

reducing agent = species oxidized: H_2, H_2, Fe.

Summary

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes $\left(\mathrm{A} = \frac{\mathrm{C}}{\mathrm{s}}\right)$, and electrical potential in volts $\left(\mathrm{V} = \frac{\mathrm{J}}{\mathrm{C}}\right)$.

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

Glossary

circuit

path taken by a current as it flows because of an electrical potential difference

current

flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\ \mathrm{A} = 1\ \frac{\mathrm{C}}{\mathrm{s}}\right)$

electrical potential

energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\ \mathrm{V} = 1\ \frac{\mathrm{J}}{\mathrm{C}}\right)$

half-reaction method

method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation “half” and reduction “half,” balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

oxidation half-reaction

the “half” of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

reduction half-reaction

the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

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5.2: Galvanic Cells

Learning Objectives

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure **5.2.1**). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \tag{5.2.1}$$

$$\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s) \tag{5.2.2}$$

$$\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq) \tag{5.2.3}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

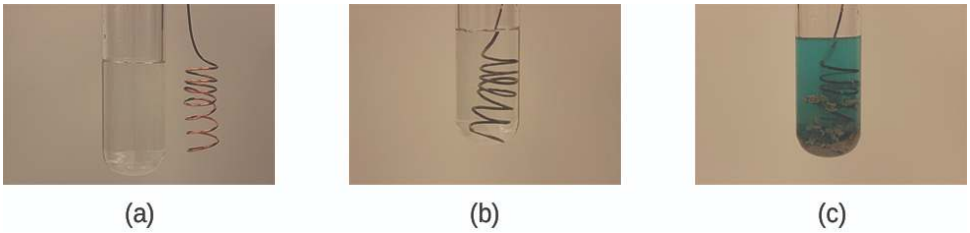


Figure **5.2.1**: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure **5.2.2**) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($AgNO_3$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the cell potential. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

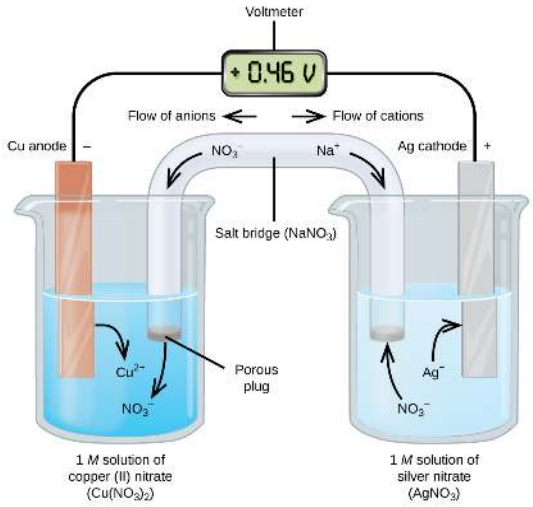


Figure **5.2.2**: In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right. There is a lot going on in Figure **5.2.2**, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The cell notation (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure **5.2.2** is then

$$\text{Cu}(s)\,|\,\text{Cu}^{2+}(aq,\,1\,M)\,\|\,\text{Ag}^{+}(aq,\,1\,M)\,|\,\text{Ag}(s)$$

Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical reactions. One such system is shown in Figure **5.2.3**. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation: } \mathrm{Mg}(s) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{e^-} \tag{5.2.4}$$

$$\text{reduction: } 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \tag{5.2.5}$$

$$\text{overall: } \mathrm{Mg}(s) + 2\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + \mathrm{H_2}(g) \tag{5.2.6}$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s)\,|\,\mathrm{Mg^{2+}}(aq)\,\|\,\mathrm{H^+}(aq)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{Pt}(s)$$

The magnesium electrode is an active electrode because it participates in the oxidation-reduction reaction. Inert electrodes, like the platinum electrode in Figure **5.2.3**, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

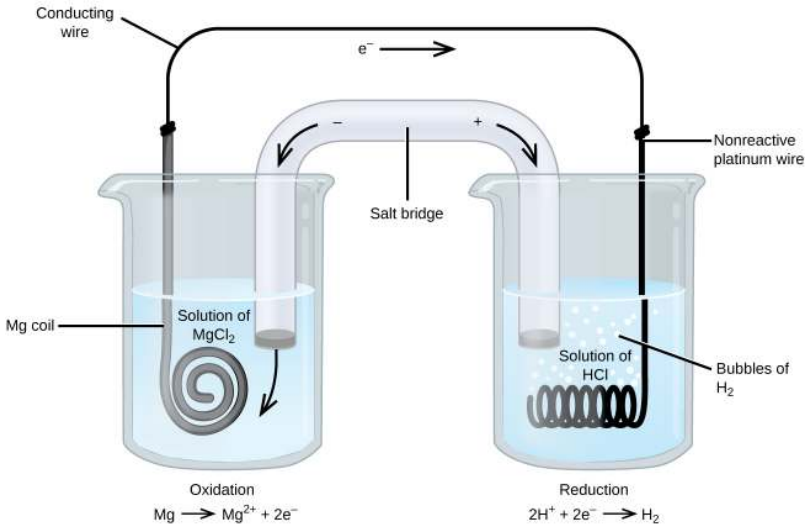


Figure **5.2.2**: The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $\mathrm{Mg} + 2\,\mathrm{H^+} \longrightarrow \mathrm{Mg^{2+}} + \mathrm{H_2}$, *which is represented in cell notation as:* $\mathrm{Mg}(s)\,|\,\mathrm{Mg^{2+}}(aq)\,\|\,\mathrm{H^+}(aq)\,|\,\mathrm{H_2}(g)\,|\,\mathrm{Pt}(s)$.

✔ Example 5.2.1: Using Cell Notation

Consider a galvanic cell consisting of

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu^{2+}}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{Cu}(s)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form $\mathrm{Cr^{3+}}$, and $\mathrm{Cu^{2+}}$ is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\text{oxidation: } 2\,\mathrm{Cr}(s) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 6\,\mathrm{e^-} \tag{5.2.7}$$

$$\text{reduction: } 3\,\mathrm{Cu^{2+}}(aq) + 6\,\mathrm{e^-} \longrightarrow 3\,\mathrm{Cu}(s) \tag{5.2.8}$$

$$\text{overall: } 2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu^{2+}}(aq) \longrightarrow 2\,\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{Cu}(s) \tag{5.2.9}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$$\mathrm{Cr}(s)\,|\,\mathrm{Cr}^{3+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Example 5.2.2: Using Cell Notation

Consider a galvanic cell consisting of

$$5\,\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^{-}(aq) + 8\,\mathrm{H}^{+}(aq) \longrightarrow 5\,\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\,\mathrm{H_2O}(l)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and $\mathrm{MnO_4}^{-}$ is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

$$\text{oxidation: } 5(\mathrm{Fe}^{2+}(aq) \longrightarrow \mathrm{Fe}^{3+}(aq) + \mathrm{e}^{-}) \tag{5.2.10}$$

$$\text{reduction: } \mathrm{MnO_4}^{-}(aq) + 8\,\mathrm{H}^{+}(aq) + 5\,\mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{2+}(aq) + 4\,\mathrm{H_2O}(l) \tag{5.2.11}$$

$$\text{overall: } 5\,\mathrm{Fe}^{2+}(aq) + \mathrm{MnO_4}^{-}(aq) + 8\,\mathrm{H}^{+}(aq) \longrightarrow 5\,\mathrm{Fe}^{3+}(aq) + \mathrm{Mn}^{2+}(aq) + 4\,\mathrm{H_2O}(l) \tag{5.2.12}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$$\mathrm{Pt}(s)\,|\,\mathrm{Fe}^{2+}(aq),\ \mathrm{Fe}^{3+}(aq)\,\|\,\mathrm{MnO_4}^{-}(aq),\ \mathrm{H}^{+}(aq),\ \mathrm{Mn}^{2+}(aq)\,|\,\mathrm{Pt}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Exercise 5.2.1

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Answer

From the information given in the problem:

$$\text{anode (oxidation): } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^{-} \tag{5.2.13}$$

$$\text{cathode (reduction): } \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^{-} \longrightarrow \mathrm{Cu}(s) \tag{5.2.14}$$

$$\text{overall: } \mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s) \tag{5.2.15}$$

Using cell notation:

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s).$$

Summary

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, ‖. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, |. The phase and concentration of the various species is included after the species name. Electrodes that participate in

the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

Glossary

active electrode
: electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

anode
: electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

cathode
: electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cell notation
: shorthand way to represent the reactions in an electrochemical cell

cell potential
: difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

galvanic cell
: electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

inert electrode
: electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

voltaic cell
: another name for a galvanic cell

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5.3: Standard Reduction Potentials

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 17.4.1 and is called the standard hydrogen electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,H^+(aq,\,1\,M) + 2\,e^- \rightleftharpoons H_2(g,\,1\text{ atm}) \quad E^\circ = 0\text{ V}$$

$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

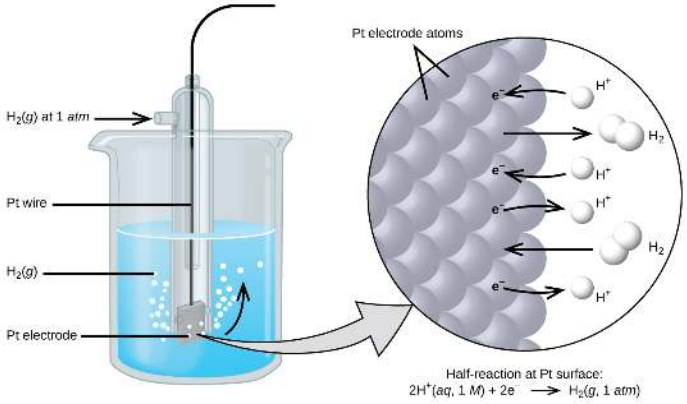


Figure **5.3.1**: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure **5.3.2**). In cell notation, the reaction is

$$Pt(s)\,|\,H_2(g,\,1\text{ atm})\,|\,H^+(aq,\,1\,M)\,\|\,Cu^{2+}(aq,\,1\,M)\,|\,Cu(s)$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}&\text{Anode (oxidation): } H_2(g) \longrightarrow 2\,H^+(aq) + 2\,e^-\\ &\text{Cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)\\ &\overline{\text{Overall: } Cu^{2+}(aq) + H_2(g) \longrightarrow 2\,H^+(aq) + Cu(s)}\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.34\text{ V} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/H_2} = E^\circ_{Cu^{2+}/Cu} - 0 = E^\circ_{Cu^{2+}/Cu}$$

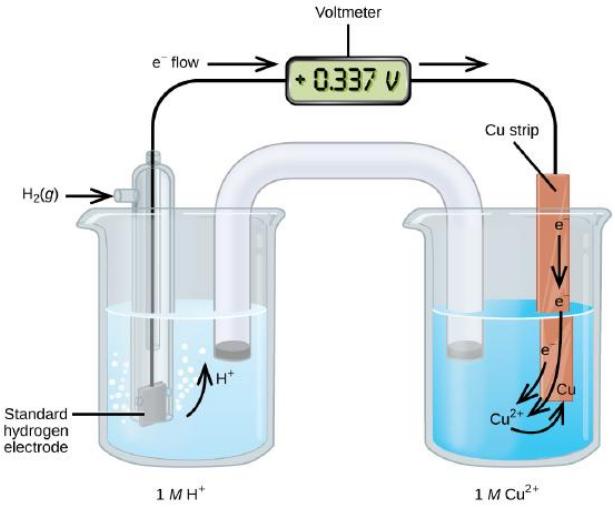


Figure **5.3.2**: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure **5.3.2**, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

Electrons flow from left to right, and the reactions are

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ &\text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ &\text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table **5.3.1**. A more complete list is provided in Tables P1 or P2.

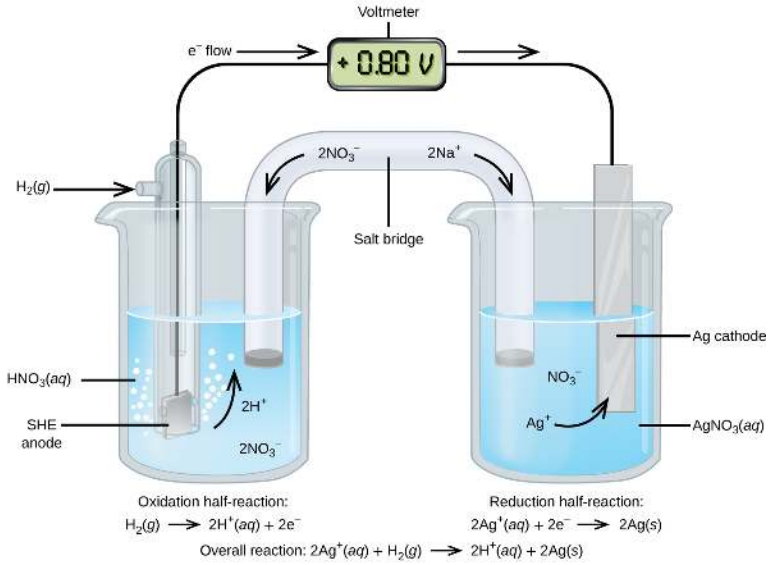


Figure **5.3.3**: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table **5.3.1**: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.69
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.507
$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.35827
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2\,e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$	+0.558
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.5355
$NiO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Ni(OH)_2(s) + 2\,OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2\,e^- \longrightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.1375
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2\,e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2\,e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$	−1.185
$Zn(OH)_2(s) + 2\,e^- \longrightarrow Zn(s) + 2\,OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.662
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71

Half-Reaction	E° (V)
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.868
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \longrightarrow K(s)$	−2.931
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Example 5.3.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of Au^{3+}/Au and Ni^{2+}/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 5.3.1, the reactions involved in the galvanic cell, both written as reductions, are

$$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E^\circ_{Au^{3+}/Au} = +1.498\ V$$

$$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s) \quad E^\circ_{Ni^{2+}/Ni} = -0.257\ V$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \quad E^\circ_{anode} = E^\circ_{Ni^{2+}/Ni} = -0.257\ V$$
$$\text{Cathode (reduction): } Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E^\circ_{cathode} = E^\circ_{Au^{3+}/Au} = +1.498\ V$$

The least common factor is six, so the overall reaction is

$$3\,Ni(s) + 2\,Au^{3+}(aq) \longrightarrow 3\,Ni^{2+}(aq) + 2\,Au(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.498\ V - (-0.257\ V) = 1.755\ V$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 5.3.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$Mg(s) + 2\,Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,Ag(s) \quad E^\circ_{cell} = 0.7996\ V - (-2.372\ V) = 3.172\ V$$

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, E°, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the

standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

Key Equations

- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

Glossary

standard cell potential (E°_{cell})

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (E°)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

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5.4: The Nernst Equation

Learning Objectives

- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

We will now extend electrochemistry by determining the relationship between E°_{cell} and the thermodynamics quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = \text{J}$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23}\ e^-}{mol} \times \frac{1.602 \times 10^{-19}\ C}{e^-} \\ &= 9.648 \times 10^4\ \frac{C}{mol} \\ &= 9.648 \times 10^4\ \frac{J}{V \cdot mol} \end{aligned}$$

Therefore

$$\text{total charge} = (\text{number of moles of e}^-) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_{ele}) by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \qquad \text{or} \qquad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele}.

$$\begin{aligned} \Delta G &= w_{\text{max}} = w_{\text{ele}} \\ &= -nFE_{\text{cell}} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{cell} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

This provides a way to relate standard cell potentials to equilibrium constants, since

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

$$-nFE^\circ_{\text{cell}} = -RT \ln K$$

or

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$
$$= \frac{\left(8.314 \ \frac{\text{J}}{\text{K·mol}}\right)(298.15 \ K)}{n \times 96,485 \ \text{C/V·mol}} \ln K$$
$$= \frac{0.0257 \ \text{V}}{n} \ln K$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., $\log_{10}$ or just log), which changes the constant by a factor of 2.303:

$$E^\circ_{\text{cell}} = \frac{0.0592 \ \text{V}}{n} \log K$$

Thus, if $\Delta G°$, K, or E°_{cell} is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 5.4.1.

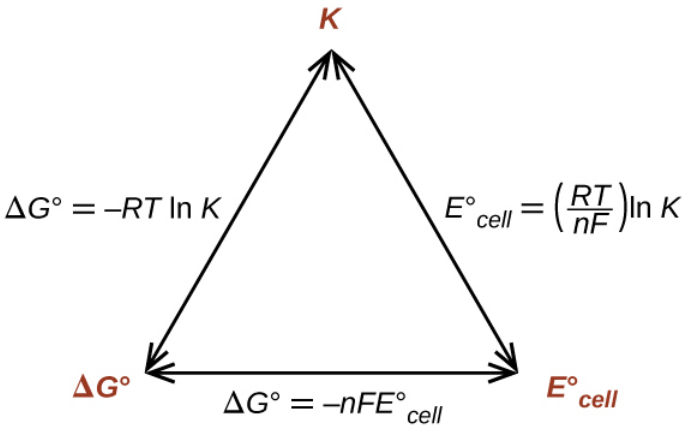


Figure 5.4.1: The relationships between ΔG°, K, and E°_{cell}. *Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.*

A diagram is shown that involves three double headed arrows positioned in the shape of an equilateral triangle. The vertices are labeled in red. The top vertex is labeled “K.“ The vertex at the lower left is labeled “delta G superscript degree symbol.” The vertex at the lower right is labeled “E superscript degree symbol subscript cell.” The right side of the triangle is labeled “E superscript degree symbol subscript cell equals (R T divided by n F) l n K.” The lower side of the triangle is labeled “delta G superscript degree symbol equals negative n F E superscript degree symbol subscript cell.” The left side of the triangle is labeled “delta G superscript degree symbol equals negative R T l n K.”

Given any one of the quantities, the other two can be calculated.

✔ Example 5.4.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?

$$2\,\text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\,\text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.

$$\text{anode (oxidation): } \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\,\text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447 \ \text{V}$$
$$\text{cathode (reduction): } 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) \qquad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7996 \ \text{V}$$
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247 \ \text{V}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With n = 2, the equilibrium constant is then

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n} \log K$$

$$\begin{aligned} K &= 10^{n \times E^\circ_{\text{cell}}/0.0592\ \text{V}} \\ &= 10^{2 \times 1.247\ \text{V}/0.0592\ \text{V}} \\ &= 10^{42.128} \\ &= 1.3 \times 10^{42} \end{aligned}$$

The standard free energy is then

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -2 \times 96,485\ \frac{\text{J}}{\text{V·mol}} \times 1.247\ \text{V} = -240.6\ \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

? Exercise 5.4.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\,\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\,\text{Cu}^{+}(aq)$$

Answer

Spontaneous; n = 2; $E^\circ_{\text{cell}} = +0.291\ \text{V}$; $\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

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

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q \tag{5.4.1}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{5.4.2}$$

Equation 5.4.2 is the generalized Nernst equation that is applicable at any temperature. However, is can be simplified for reactions occuring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257\ \text{V}}{n} \ln Q \tag{5.4.3}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n} \log_{10} Q \tag{5.4.4}$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation5.4.2. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

✔ Example 5.4.2: Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

$$\text{Co}(s) + \text{Fe}^{2+}(aq,\ 1.94\ M) \longrightarrow \text{Co}^{2+}(aq,\ 0.15\ M) + \text{Fe}(s)$$

Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,

$$\begin{aligned}&\text{Anode (oxidation): } \mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2\,\mathrm{e}^- \qquad E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}} = -0.28\ \mathrm{V}\\ &\text{Cathode (reduction): } \mathrm{Fe}^{2+}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Fe}(s) \qquad E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.447\ \mathrm{V}\\ &E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447\ \mathrm{V} - (-0.28\ \mathrm{V}) = -0.17\ \mathrm{V}\end{aligned}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

$$Q = \frac{[Co^2+]}{[Fe^2+]} = \frac{0.15\ M}{1.94\ M} = 0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 5.4.4)

$$\begin{aligned}E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592\ \mathrm{V}}{n}\log Q\\ &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log 0.077\\ &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} = -0.14\ \mathrm{V}\end{aligned}$$

The process is (still) nonspontaneous.

? Exercise 5.4.2

What is the cell potential for the following reaction at room temperature?

$$\mathrm{Al}(s)\,|\,\mathrm{Al}^{3+}(aq,\ 0.15\ M)\,\|\,\mathrm{Cu}^{2+}(aq,\ 0.025\ M)\,|\,\mathrm{Cu}(s)$$

What are the values of *n* and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer

n = 6; *Q* = 1440; E_{cell} = +1.97 V, spontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

✓ Example 5.4.3: Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq,\ 0.10\ M)\,\|\,\mathrm{Zn}^{2+}(aq,\ 0.50\ M)\,|\,\mathrm{Zn}(s)$$

Solution

From the information given:

$$\begin{aligned}&\text{Anode: } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) + 2\,\mathrm{e}^- \qquad E^\circ_{\text{anode}} = -0.7618\ \mathrm{V}\\ &\text{Cathode: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}(s) \qquad E^\circ_{\text{cathode}} = -0.7618\ \mathrm{V}\\ &\hline\\ &\text{Overall: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) \qquad E^\circ_{\text{cell}} = 0.000\ \mathrm{V}\end{aligned}$$

The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{cell} = 0.000\ V - \frac{0.0592\ V}{2} \log \frac{0.10}{0.50} = +0.021\ V$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1. $Q < 1$ in this case, so the process is spontaneous.

? Exercise 5.4.3

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 M, what was the concentration at the anode?

Answer

Q = 0.00042; $[Zn^{2+}]_{cat}$ = 2.1 \times 10^{-4} M.

Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant (F = 96,485 C/mol e^-). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

Key Equations

- $E^\circ_{cell} = \frac{RT}{nF} \ln K$
- $E^\circ_{cell} = \frac{0.0257\ V}{n} \ln K = \frac{0.0592\ V}{n} \log K \quad (\text{at } 298.15\ K)$
- $E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q \quad (\text{Nernst equation})$
- $E_{cell} = E^\circ_{cell} - \frac{0.0257\ V}{n} \ln Q = E^\circ_{cell} - \frac{0.0592\ V}{n} \log Q \quad (\text{at } 298.15\ K)$
- $\Delta G = -nFE_{cell}$
- $\Delta G^\circ = -nFE^\circ_{cell}$
- $w_{ele} = w_{max} = -nFE_{cell}$

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (F)

charge on 1 mol of electrons; F = 96,485 C/mol e^-

Nernst equation

equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

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5.5: Batteries and Fuel Cells

Learning Objectives

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

> *Visit this site to learn more about batteries.*

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure 5.5.1). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) + 2\,\mathrm{e^-} \quad E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.7618\ \mathrm{V}$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.



Figure 5.5.1: The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell.

A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface of the cylinder, indicated as a thin red line, is labeled "zinc can (electrode)." Just beneath this is a slightly thicker dark grey surface that covers the lateral surface, top, and bottom of the battery, which is labeled "Porous separator." Inside is a purple region with many evenly spaced small darker purple dots, labeled "Paste of M n O subscript 2, N H subscript 4 C l, Z n C l subscript 2, water (cathode)." A dark grey rod, labeled "Carbon rod (electrode)," extends from the top of the battery, leaving a gap of less than one-fifth the height of the battery below the rod to the bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled "Metal bottom cover (negative)." The very top of the cylinder has a thin grey surface that curves upward at the center over the top of the carbon electrode at the center of the cylinder. This upper surface is labeled "Metal top cover (positive)." A thin dark grey line just below this surface is labeled "Insulator." Below this, above the purple region, and outside of the carbon electrode at the center is an orange region that is labeled "Seal."

Alkaline batteries (Figure 5.5.2) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{aligned}
&\text{anode: } \mathrm{Zn}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} \qquad E^\circ_{\text{anode}} = -1.28\ \mathrm{V} \\
&\underline{\text{cathode: } 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{OH^-}(aq) \qquad E^\circ_{\text{cathode}} = +0.15\ \mathrm{V}} \\
&\text{overall: } \mathrm{Zn}(s) + 2\,\mathrm{MnO_2}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) \qquad E^\circ_{\text{cell}} = +1.43\ \mathrm{V}
\end{aligned}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

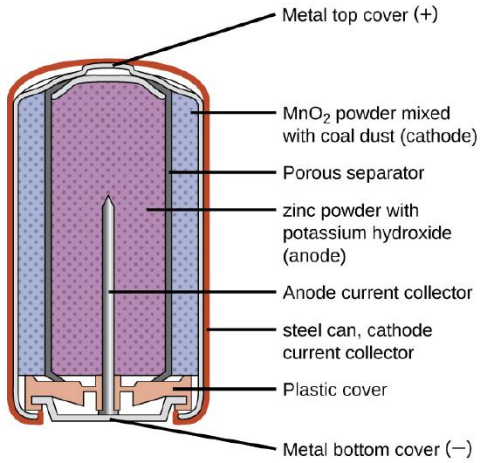


Figure 5.5.2: Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries.

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure 5.5.3) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{aligned}
&\text{anode: } \mathrm{Cd}(s) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Cd(OH)_2}(s) + 2\,\mathrm{e^-} \\
&\underline{\text{cathode: } \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni(OH)_2}(s) + 2\,\mathrm{OH^-}(aq)} \\
&\text{overall: } \mathrm{Cd}(s) + \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cd(OH)_2}(s) + \mathrm{Ni(OH)_2}(s)
\end{aligned}$$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

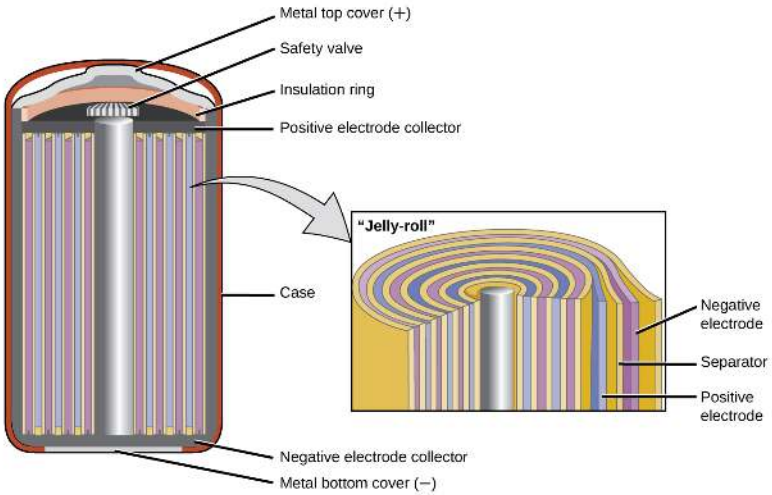


Figure 5.5.3: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 5.5.4) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{aligned}&\text{anode: } \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-}\\ &\text{cathode: } x\mathrm{Li^+} + x\mathrm{e^-} + x\mathrm{C_6} \rightleftharpoons x\mathrm{LiC_6}\\ \hline &\text{overall: } \mathrm{LiCoO_2} + x\mathrm{C_6} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{LiC_6}\end{aligned}$$

With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

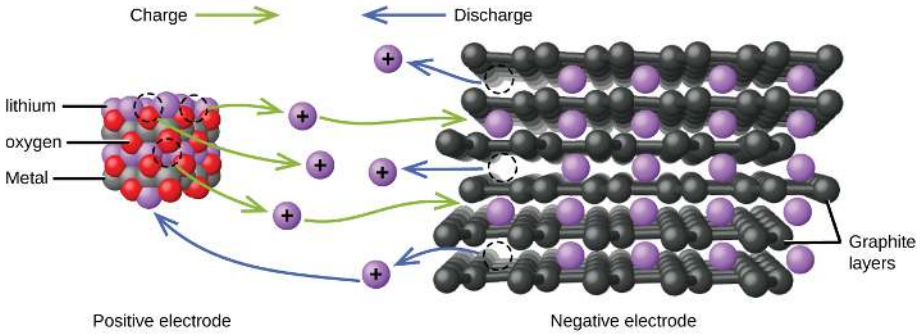


Figure 5.5.4: In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

The lead acid battery (Figure 5.5.5) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{aligned}&\text{anode: } \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode: } \mathrm{PbO_2}(s) + \mathrm{HSO_4^-}(aq) + 3\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)\\ \hline &\text{overall: } \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \longrightarrow 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)\end{aligned}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

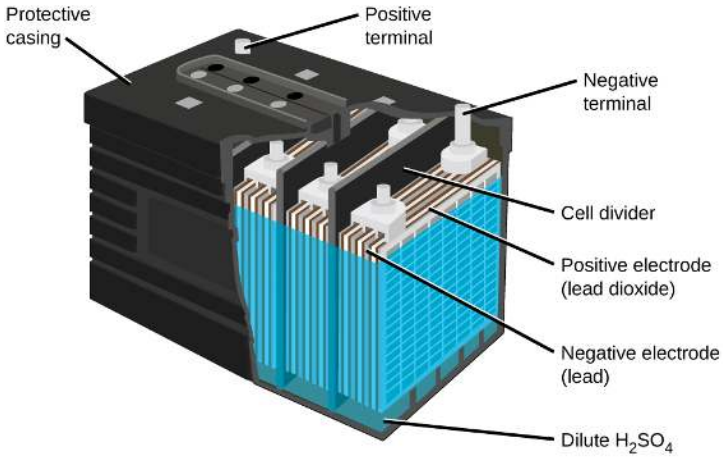


Figure **5.5.5**: The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

Fuel Cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure **5.5.6**).

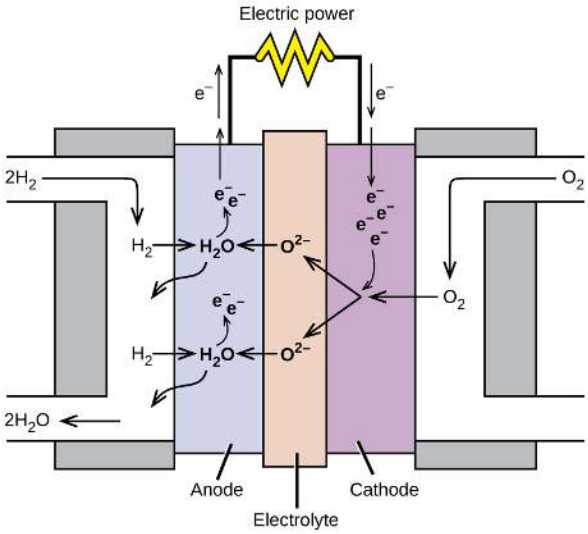


Figure **5.5.6**: In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are

$$\text{anode: } 2\,H_2 + 2\,O^{2-} \longrightarrow 2\,H_2O + 4\,e^-$$
$$\text{cathode: } O_2 + 4\,e^- \longrightarrow 2\,O^{2-}$$
$$\text{overall: } 2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Summary

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of

primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

Summary

alkaline battery

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

nickel-cadmium battery

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

primary battery

single-use nonrechargeable battery

secondary battery

battery that can be recharged

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5.6: Corrosion

Learning Objectives

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathbf{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \underset{\text{red}}{\mathrm{Cu_2O\,(s)}}$$

$$\mathrm{Cu_2O\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow 2\,\underset{\text{black}}{\mathrm{CuO\,(s)}}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the $\mathbf{CuO}$.

$$2\,\mathrm{CuO\,(s)} + \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2\,(s)}}$$

$$3\,\mathrm{CuO\,(s)} + 2\,\mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2\,(s)}}$$

$$4\,\mathrm{CuO\,(s)} + \mathrm{SO_3\,(g)} + 3\,\mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6\,(s)}}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.

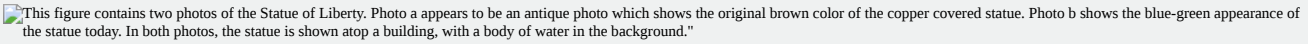

This figure contains two photos of the Statue of Liberty. Photo a appears to be an antique photo which shows the original brown color of the copper covered statue. Photo b shows the blue-green appearance of the statue today. In both photos, the statue is shown atop a building, with a body of water in the background."

Figure **5.6.1**: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: } \mathrm{Fe_{(s)}} \rightarrow \mathrm{Fe^{2+}{}_{(aq)}} + 2\,\mathrm{e^-} \quad E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: } \mathrm{O_{2(g)}} + 4\,\mathrm{H^+{}_{(aq)}} + 4\,\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O_{(l)}} \quad E^\circ_{\mathrm{O_2/O_2}} = +1.23\ \mathrm{V}$$

$$\text{overall: } 2\,\mathrm{Fe_{(s)}} + \mathrm{O_{2(g)}} + 4\,\mathrm{H^+{}_{(aq)}} \rightarrow 2\,\mathrm{Fe^{2+}{}_{(aq)}} + 2\,\mathrm{H_2O_{(l)}} \quad E^\circ_{\text{cell}} = +1.67\ \mathrm{V}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\,\mathrm{Fe^{2+}{}_{(aq)}} + \mathrm{O_{2(g)}} + (4+2x)\mathrm{H_2O_{(l)}} \rightarrow 2\,\mathrm{Fe_2O_3 \cdot}\,x\mathrm{H_2O_{(s)}} + 8\,\mathrm{H^+{}_{(aq)}}$$

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

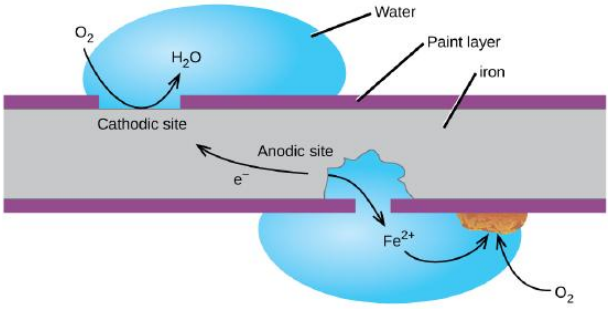


Figure **5.6.2**: Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

A grey rectangle, labeled “iron,” is shown with thin purple layers, labeled “Paint layer,” at its upper and lower surfaces. A gap in the upper purple layer at the upper left of the diagram is labeled “Cathodic site.” A blue droplet labeled “water” is positioned on top of the gap. A curved arrow extends from a space above the droplet to the surface of the grey region and into the water droplet. The base of the arrow is labeled “O subscript 2” and the tip of the arrow is labeled “H subscript 2 O.” A gap to the right and on the bottom side of the grey region shows that some of the grey region is gone from the region beneath the purple layer. A water droplet covers this gap and extends into the open space in the grey rectangle. The label “F e superscript 2 positive” is at the center of the droplet. A curved arrow points from the edge of the grey area below to the label. A second curved arrow extends from the F e superscript 2 positive arrow to a rust brown chunk on the lower surface of the purple layer at the edge of the water droplet. A curved arrow extends from O subscript 2 outside the droplet into the droplet to the rust brown chunk. The grey region at the lower right portion of the diagram is labeled “Anodic site.” An arrow extends from the anodic site toward the cathodic site, which is labeled “e superscript negative.”

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.



Figure **5.6.3**: One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

A diagram is shown of an underground storage tank system. Underground, to the left end of the diagram is a horizontal grey tank which is labeled “Object to be protected.” A black line extends upward from the center of the tank above ground. An arrow points upward at the left side of the line segment. A horizontal black line segment continues right above ground, which is labeled “No power source is needed.” A line segment extends up and to the right, which is labeled “ Lead wire.” A line segment with a downward pointing arrow to its right extends downward below the ground to a second metal tank-like structure, labeled “Sacrificial anode” which is vertically oriented. Five black arrows point left underground toward the first tank. These arrows are collectively labeled “Protective current.”

Another important way to protect metal is to make it the cathode in a galvanic cell. This is cathodic protection and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium. This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called sacrificial anodes because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

Summary

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode

in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The “protected” metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

Glossary

cathodic protection
: method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

corrosion
: degradation of metal through an electrochemical process

galvanized iron
: method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

sacrificial anode
: more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

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5.7: Electrolysis

Learning Objectives

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In electrolytic cells, electrical energy causes nonspontaneous reactions to occur in a process known as electrolysis. The charging electric barttery shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile. The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure **5.7.1**. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode: } 2\,Cl^-(l) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{Cl_2/Cl^-} = +1.3\,V \tag{5.7.1}$$

$$\text{cathode: } Na^+(l) + e^- \longrightarrow Na(l) \quad E^\circ_{Na^+/Na} = -2.7\,V \tag{5.7.2}$$

$$\text{overall: } 2\,Na^+(l) + 2\,Cl^-(l) \longrightarrow 2\,Na(l) + Cl_2(g) \quad E^\circ_{cell} = -4.0\,V \tag{5.7.3}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

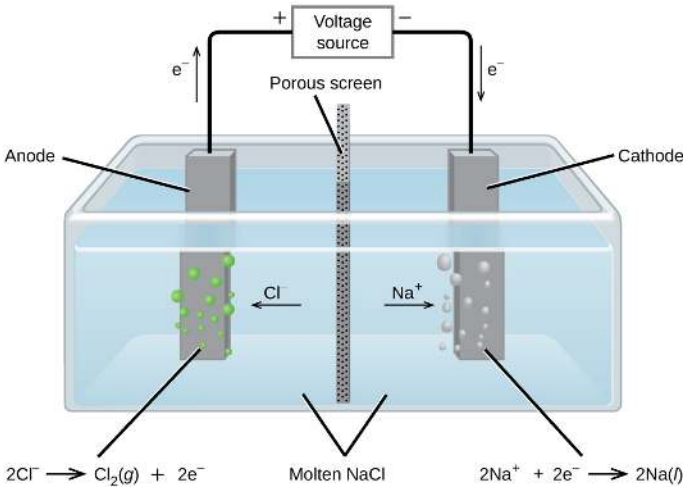


Figure **5.7.1**: Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure **5.7.2**). The reactions are

$$\text{anode: } 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{anode} = +1.229\,V \tag{5.7.4}$$

$$\text{cathode: } 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{cathode} = 0\,V \tag{5.7.5}$$

$$\text{overall: } 2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g) \quad E^\circ_{cell} = -1.229\,V \tag{5.7.6}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

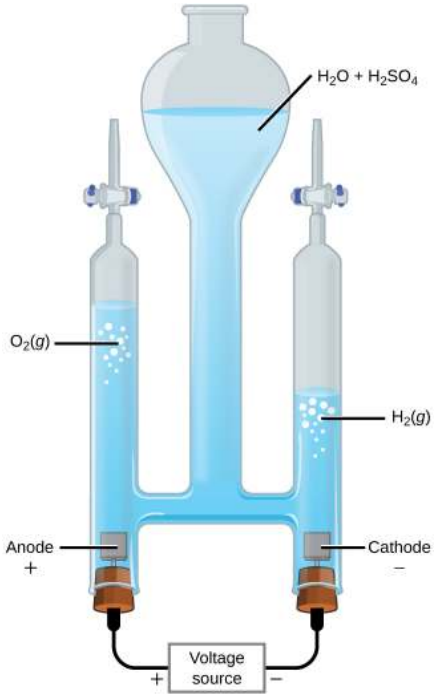


Figure **5.7.2**: Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i) } 2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- \quad E^\circ_{anode} = +1.35827\ V \tag{5.7.7}$$
$$\text{(ii) } 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad E^\circ_{anode} = +1.229\ V \tag{5.7.8}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The overpotential is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii) } 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad E^\circ_{cathode} = 0\ V \tag{5.7.9}$$
$$\text{(iv) } 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \quad E^\circ_{cathode} = -0.8277\ V \tag{5.7.10}$$
$$\text{(v) } Na^+(aq) + e^- \longrightarrow Na(s) \quad E^\circ_{cathode} = -2.71\ V \tag{5.7.11}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only 1×10^{-7} *M*. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$\text{overall: } 2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq) \quad E^\circ_{cell} = -2.186\ V$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure **5.7.3**).

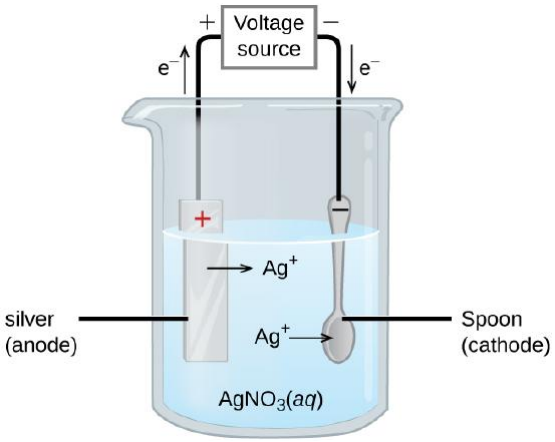


Figure **5.7.3**: The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\textbf{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{e^-}$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\textbf{cathode: } \mathrm{Ag^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second ($1\ \mathrm{A} = 1\ \frac{\mathrm{C}}{\mathrm{s}}$). The total charge ($Q$, in coulombs) is given by

$$Q = I \times t = n \times F$$

where

- t is the time in seconds,
- n the number of moles of electrons, and
- F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 5.7.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\ \text{C}}{\text{s}} \times 1\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{60\ \text{s}}{\text{min}}}{96,485\ \text{C/mol e}^-} = \frac{36,830\ \text{C}}{96,485\ \text{C/mol e}^-} = 0.3817\ \text{mol e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } Ag^+(aq) + e^- \longrightarrow Ag(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817\ \text{mol e}^- \times \frac{1\ \text{mol Ag}}{1\ \text{mol e}^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 41.19\ \text{g Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

Exercise 5.7.1

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer

$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$; 7.77 mol Al = 210.0 g Al.

Example 5.7.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume} = \left(0.010\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}}\right) \times \left(3.3\ \text{m}^2 \times \left(\frac{10,000\ \text{cm}^2}{1\ \text{m}^2}\right)\right) = 33\ \text{cm}^3$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass} = \text{volume} \times \text{density} = 33\ \cancel{\text{cm}^3} \times \frac{7.19\ \text{g}}{\cancel{\text{cm}^3}} = 237\ \text{g Cr}$$

$$\text{mol Cr} = 237\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} = 4.56\ \text{mol Cr}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\ \text{mol Cr} \times \frac{3\ \text{mol e}^-}{1\ \text{mol Cr}} \times \frac{96485\ \text{C}}{\text{mol e}^-} = 1.32 \times 10^6\ \text{C}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\ \text{C}}{33.46\ \text{C/s}} = 3.95 \times 10^4\ \text{s} = 11.0\ \text{hr}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

? Exercise 5.7.2

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

231 g Zn required 23,000 minutes.

Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

Summary

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating

depositing a thin layer of one metal on top of a conducting surface

overpotential

difference between the theoretical potential and actual potential in an electrolytic cell; the “extra” voltage required to make some nonspontaneous electrochemical reaction to occur

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5.E: Electrochemistry (Exercises)

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CHAPTER OVERVIEW

6: Thermodynamics

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General Chemistry

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

6.1: Spontaneity

6.2: Entropy

6.3: The Second and Third Laws of Thermodynamics

6.4: Gibbs Energy

6.E: Thermodynamics (Exercises)

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6.1: Spontaneity

Learning Objectives

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

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

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **6.1.1**).

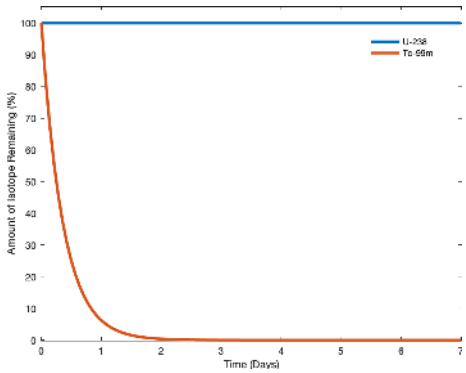


Figure **6.1.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure **6.1.2**).

$$\mathbf{C(s, diamond) \longrightarrow C(s, graphite)} \tag{6.1.1}$$

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.

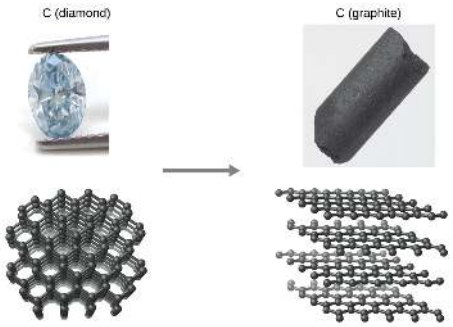


Figure **6.1.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure **6.1.3**). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{6.1.2}$$

$$= 0 \ \ (\mathbf{P = 0 \ in \ a \ vaccum}) \tag{6.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (6.1.4)$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

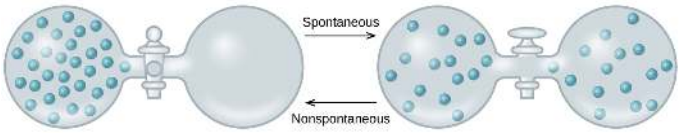


Figure **6.1.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

When the valve is closed, all of the gas molecules accumulating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure **6.1.4**). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (6.1.5)$$

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



Figure **6.1.4**:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

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

✔ Example **6.1.1**: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

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

Solution



Figure **6.1.5**:(credit a: modification of work by Jenny Downing; credit b: modification of work by "Fuzzy Gerdes"/Flickr; credit c: modification of work by Sahar Atwa)

This figure has three photos labeled, "a," "b," and "c." Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

? Exercise **6.1.1**

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

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
: process that requires continual input of energy from an external source

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

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6.2: Entropy

Learning Objectives

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

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure **6.2.2**) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

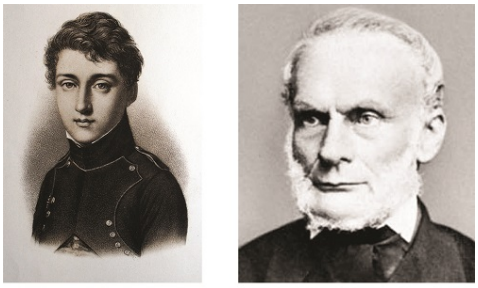


Figure **6.2.1**: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{rev}}{T} \tag{6.2.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{6.2.2}$$

Here k is the Boltzmann constant and has a value of $1.38 \times 10^{-23}\ J/K$.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\begin{aligned} \Delta S &= S_f - S_i \\ &= k \ln \Omega_f - k \ln \Omega_i \\ &= k \ln \frac{\Omega_f}{\Omega_i} \end{aligned} \tag{6.2.3}$$

For processes involving an increase in the number of microstates of the system, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $\Omega_f < \Omega_i$, yield a decrease in system entropy, ΔS

< 0. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

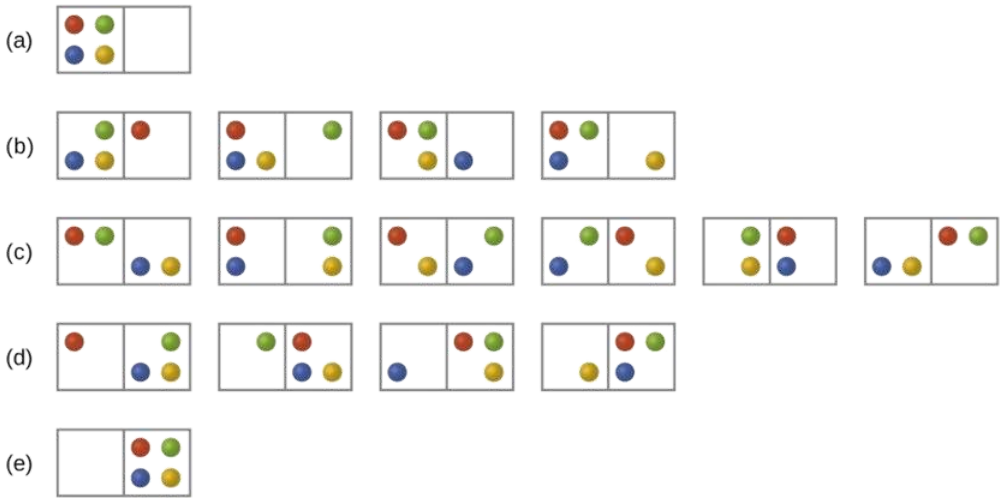


Figure **6.2.2**: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

Five rows of diagrams that look like dominoes are shown and labeled a, b, c, d, and e. Row a has one "domino" that has four dots on the left side, red, green, blue and yellow in a clockwise pattern from the top left, and no dots on the right. Row b has four "dominos," each with three dots on the left and one dot on the right. The first shows a "domino" with green, yellow and blue on the left and red on the right. The second "domino" has yellow, blue and red on the left and green on the right. The third "domino" has red, green and yellow on the left and blue on the right while the fourth has red, green and blue on the left and yellow on the right. Row c has six "dominos", each with two dots on either side. The first has a red and green on the left and a blue and yellow on the right. The second has a red and blue on the left and a green and yellow on the right while the third has a yellow and red on the left and a green and blue on the right. The fourth has a green and blue on the left and a red and yellow on the right. The fifth has a green and yellow on the left and a red and blue on the right. The sixth has a blue and yellow on the left and a green and red on the right. Row d has four "dominos," each with one dot on the left and three on the right. The first "domino" has red on the left and a blue, green and yellow on the right. The second has a green on the left and a red, yellow and blue on the right. The third has a blue on the left and a red, green and yellow on the right. The fourth has a yellow on the left and a red, green and blue on the right. Row e has 1 "domino" with no dots on the left and four dots on the right that are red, green, blue and yellow.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in $2^4 = 16$ different microstates as illustrated in Figure **6.2.2**. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

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

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

> *The most probable distribution is therefore the one of greatest entropy.*

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

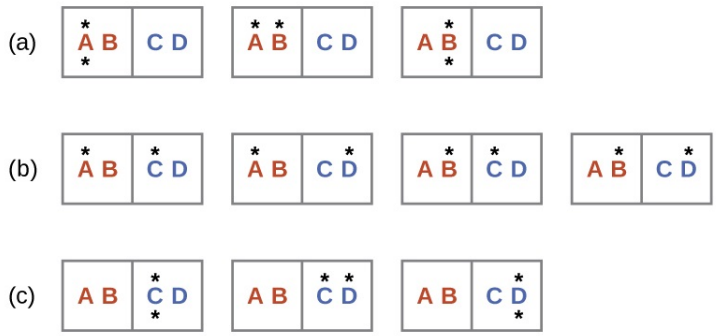


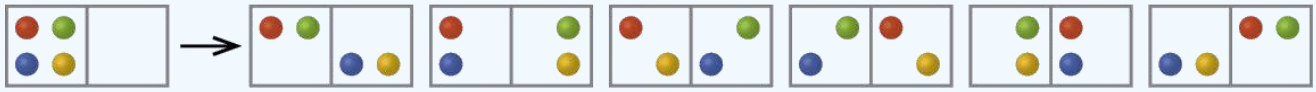
Figure **6.2.3**: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Three rows labeled a, b, and c are shown and each contains rectangles with two sides where the left side is labeled, “A,” and “B,” and the right is labeled, “C,” and “D.” Row a has three rectangles where the first has a dot above and below the letter A, the second has a dot above the A and B, and the third which has a dot above and below the letter B. Row b has four rectangles; the first has a dot above A and C, the second has a dot above A and D, the third has a dot above B and C and the fourth has a dot above B and D. Row c has three rectangles; the first has a dot above and below the letter C, the second has a dot above C and D and the third has a dot above and below the letter D.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as “*”) in Figure **6.2.3**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects’ temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

✔ Example 6.2.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



A diagram shows one rectangle with two sides that has four dots, red, green, yellow and blue written on the left side. A right-facing arrow leads to six more two-sided rectangles, each with two dots on the left and right sides. The first rectangle has a red and green dot on the left and a blue and yellow on the right, while the second shows a red and blue on the left and a green and yellow on the right. The third rectangle has a red and yellow dot on the left and a blue and green on the right, while the fourth shows a green and blue on the left and a red and yellow on the right. The fifth rectangle has a yellow and green dot on the left and a blue and red on the right, while the sixth shows a yellow and blue on the left and a green and red on the right.

Solution

We are interested in the following change:

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

$$\Delta S = k \ln \frac{\Omega_c}{\Omega_a}$$

$$= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1}$$

$$= 2.47 \times 10^{-23}\ J/K$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

? Exercise 6.2.1

Consider the system shown in Figure **6.2.3**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure **6.2.4**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

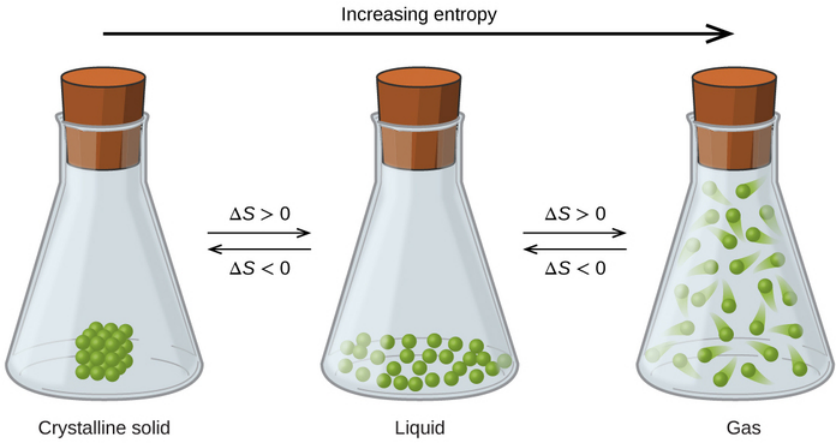


Figure **6.2.4**: The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid.

Three stoppered flasks are shown with right and left-facing arrows in between each; the first is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0,” while the second is labeled above as, “delta S greater than 0,” and below as, “delta S less than 0.” A long, right-facing arrow is drawn above all the flasks and labeled, “Increasing entropy.” The left flask contains twenty-seven particles arranged in a cube in the bottom of the flask and is labeled, “Crystalline solid,” below. The middle flask contains twenty-seven particles dispersed randomly in the bottom of the flask and is labeled, “Liquid,” below. The right flask contains twenty-seven particles dispersed inside of the flask and moving rapidly and is labeled, “Gas,” below.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure **6.2.5**).

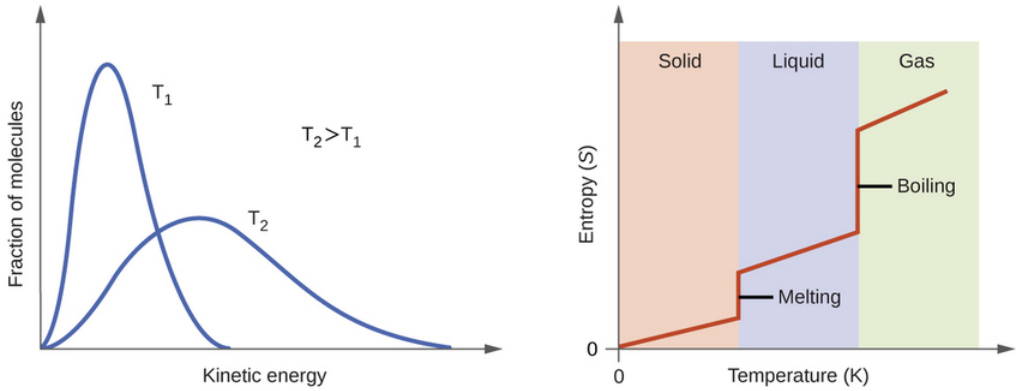


Figure 6.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

Two graphs are shown. The y-axis of the left graph is labeled, “Fraction of molecules,” while the x-axis is labeled, “Velocity, v (m / s),” and has values of 0 through 1,500 along the axis with increments of 500. Four lines are plotted on this graph. The first, labeled, “100 K,” peaks around 200 m / s while the second, labeled, “200 K,” peaks near 300 m / s and is slightly lower on the y-axis than the first. The third line, labeled, “500 K,” peaks around 550 m / s and is lower than the first two on the y-axis. The fourth line, labeled, “1000 K,” peaks around 750 m / s and is the lowest of the four on the y-axis. Each line get increasingly broad. The second graph has a y-axis labeled, “Entropy, S,” with an upward-facing arrow and an x-axis labeled, “Temperature (K),” and a right-facing arrow. The graph has three equally spaced columns in the background, labeled, “Solid,” “Liquid,” and, “Gas,” from left to right. A line extends slightly upward through the first column in a slight upward direction, then goes straight up in the transition between the first two columns. In then progresses in a slight upward direction through the second column, then goes up dramatically between the second and third columns, then continues in a slight upward direction once more. The first vertical region of this line is labeled, “Melting,” and the second is labeled, “Boiling.”

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle’s mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

✔ Example 6.2.2: Predicting the Sign of ΔS

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

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C

b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$

c. $\mathrm{C_6H_6}(l) + \frac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\,\mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$

d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases

b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

c. negative, net decrease in the amount of gaseous species

d. positive, phase transition from solid to liquid, net increase in dispersal of matter

? Exercise 6.2.2

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

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

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas

Answer d

Positive; There is a net production of one mole of gas.

Summary

Entropy (\(S\)) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$

Glossary

entropy (S)
state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (W)
possible configuration or arrangement of matter and energy within a system

reversible process
process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

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6.3: The Second and Third Laws of Thermodynamics

Learning Objectives

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

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{6.3.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{6.3.2}$$

   The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{6.3.3}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table **6.3.1**.

Table **6.3.1**: The Second Law of Thermodynamics

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

All spontaneous changes cause an increase in the entropy of the universe.

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{6.3.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example **6.3.1**.

✔ Example 6.3.1: Will Ice Spontaneously Melt?

The entropy change for the process

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

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

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

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

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

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

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

? Exercise 6.3.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and

complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0 \tag{6.3.5}$$

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

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S°_{298} for values determined for one mole of substance, isolated in its pure form in its own container, at a pressure of 1 bar and a temperature of 298 K.

Definition: Term

The thermodynamic standard state of a substance refers to an isolated sample of that substance, in its own container, at 1.000 bar (0.9869 atm) pressure. If the substance is a solute, the most common standard state is one in which the concentration of the solute is 1.000 molal (sometimes approximated with 1.000 M). There is no defined temperature for the standard state, but most discussions about standard state assume that the temperature is 298.15 K (25ºC) unless otherwise noted.

This may seem like a strange definition, because it requires that each of the reactants and each of the products of a reaction are kept separate from one another, unmixed. The entropy of mixing must be determined separately.

The standard entropy change ($\Delta S°$) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^\circ = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \tag{6.3.6}$$

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

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{6.3.7}$$

is computed as the following:

$$= [xS^\circ_{298}(\text{C}) + yS^\circ_{298}(\text{D})] - [mS^\circ_{298}(\text{A}) + nS^\circ_{298}(\text{B})] \tag{6.3.8}$$

Table **6.3.2** lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 or T2.

Table **6.3.2**: Standard Entropies (at 298.15 K, 1 atm)

Substance	$S^\circ_{298}\ \frac{J}{mol\ K}$
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
H(*g*)	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(*g*)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 6.3.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

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

Solution

The value of the standard entropy change at room temperature, ΔS°_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^\circ_{298} &= S^\circ_{298}(\mathbf{H_2O}(l)) - S^\circ_{298}(\mathbf{H_2O}(g)) \\ &= (70.0\ J\ mol^{-1}K^{-1}) - (188.8\ J mol^{-1}K^{-1}) = -118.8\ J\ mol^{-1}K^{-1}\end{aligned}$$

The value for ΔS°_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 6.3.2

Calculate the standard entropy change for the following process:

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

Answer

$-120.6\ \text{J mol}^{-1}\ \text{K}^{-1}$

Example 6.3.3: Determination of ΔS°

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

$$2\,\text{CH}_3\text{OH}(l) + 3\,\text{O}_2(g) \longrightarrow 2\,\text{CO}_2(g) + 4\,\text{H}_2\text{O}(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients.

$$\begin{aligned}\Delta S^\circ = \Delta S^\circ_{298} &= \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \\ &= [2S^\circ_{298}(\text{CO}_2(g)) + 4S^\circ_{298}(\text{H}_2\text{O}(l))] - [2S^\circ_{298}(\text{CH}_3\text{OH}(l)) + 3S^\circ_{298}(\text{O}_2(g))] \\ &= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1\ J/mol \cdot K\end{aligned}$$

Exercise 6.3.3

Calculate the standard entropy change for the following reaction:

$$\text{Ca(OH)}_2(s) \longrightarrow \text{CaO}(s) + \text{H}_2\text{O}(l)$$

Answer

24.7 J/mol•K

Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$

Glossary

second law of thermodynamics
entropy of the universe increases for a spontaneous process

standard entropy (S°)
entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

standard entropy change (ΔS°)
change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

third law of thermodynamics
entropy of a perfect crystal at absolute zero (0 K) is zero

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6.4: 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:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{6.4.1}$$

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 **6.4.1** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table **6.4.1**: 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 **6.4.1**.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6.4.2}$$

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 6.4.1: 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:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{6.4.3}$$

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

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ \tag{6.4.4}$$

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:

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

then use Equation 6.4.2:

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

Converting everything into kJ and combining at 298 K:

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

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

? Exercise 6.4.1: 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

$\Delta G^\circ_{298} = \mathrm{102.0\ kJ/mol}$; 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 (ΔG°_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, (ΔG°_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

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{6.4.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\mathrm{products}) - \sum \nu \Delta G^\circ_{298}(\mathrm{reactants}) \tag{6.4.6}$$

$$= [x\Delta G^\circ_f(\mathrm{C}) + y\Delta G^\circ_f(\mathrm{D})] - [m\Delta G^\circ_f(\mathrm{A}) + n\Delta G^\circ_f(\mathrm{B})]. \tag{6.4.7}$$

✓ Example 6.4.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

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

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	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S_{298}° (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

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

(b) Using enthalpies and entropies of formation:

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

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 6.4.2

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?

$$C_2H_4(g) \longrightarrow H_2(g) + C_2H_2(g)$$

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 **6.4.1**

Table **6.4.1**

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 6.4.3: Predicting the Temperature Dependence of Spontaneity

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

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

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

Solution

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

Exercise 6.4.3

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

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

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

Answer

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

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, it is important to keep in mind what the terms “high” and “low” mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in “extent” (as reflected by its ΔG^o) as temperature varies.

This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the *y* axis versus *T* on the *x* axis:

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

$$y = b + mx$$

Such a plot is shown in Figure **6.4.2**. 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:

$$\Delta G^o = 0 = \Delta H^o - T\Delta S^o$$

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

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

Note

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

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

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

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

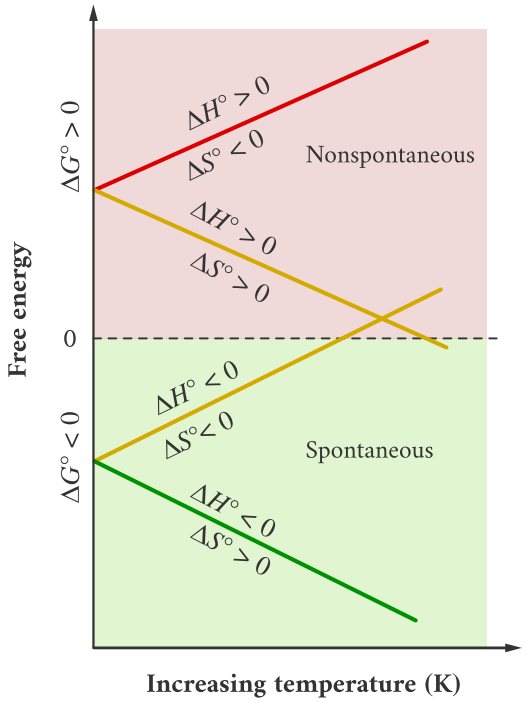


Figure **6.4.2**: These plots show the variation in ΔGº with temperature for the four possible combinations of arithmetic sign for ΔHº and ΔSº. Note that in this graph of ΔGº, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example **6.4.4**: 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,

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

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

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

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 6.4.4

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:

$$\Delta G = \Delta G° + RT \ln Q \tag{6.4.8}$$

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 6.4.1.

Example 6.4.5: Calculating ΔG under Nonstandard Conditions

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

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

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

Solution

Equation 6.4.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

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

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 6.4.5

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 6.4.8 may be written as

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

$$\Delta G^\circ = -RT\ln K \tag{6.4.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{6.4.10}$$

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 6.4.1.

Table 6.4.1: 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 6.4.6: 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:

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

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

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

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 6.4.10:

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

Exercise 6.4.6: 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.

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

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 **6.4.3**). 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.

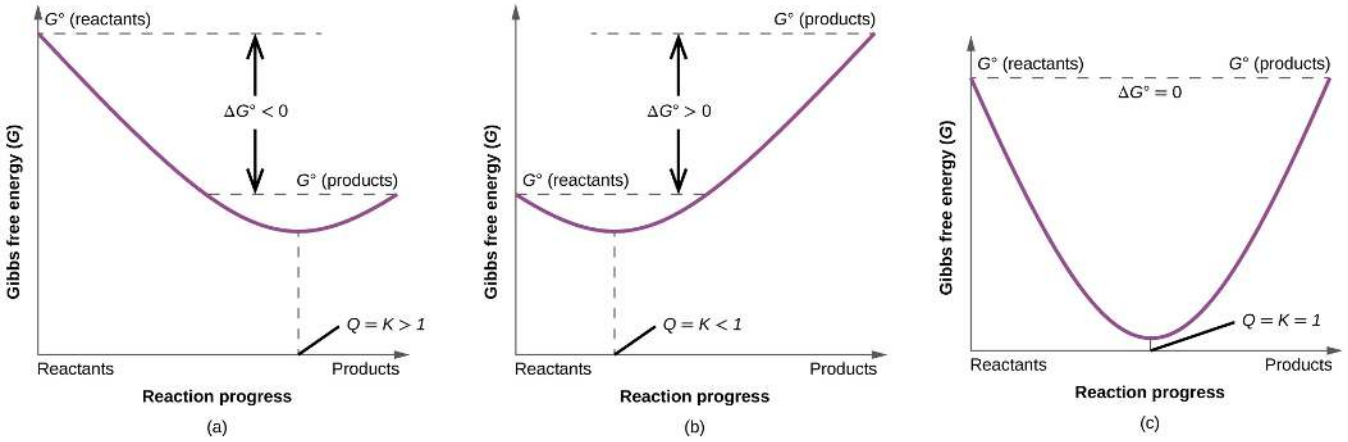


Figure **6.4.3**: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note 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 ΔG indicates that the process will proceed in the forward direction to reach equilibrium; a positive ΔG indicates that the process will proceed in the reverse direction to reach equilibrium ; and a ΔG of zero indicates that the system is at equilibrium. A negative value for ΔG^o means that the reaction is product-favored at equilibrium. A positive value for ΔG^o means that the reaction is reactant-favored at equilibrium. If ΔG^o 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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6.E: Thermodynamics (Exercises)

16.1: Spontaneity Exercises

Q16.1.1

What is a spontaneous reaction?

S16.1.1

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

Q16.1.2

What is a nonspontaneous reaction?

Q16.1.3

Indicate whether the following processes are spontaneous or nonspontaneous.

a. Liquid water freezing at a temperature below its freezing point
b. Liquid water freezing at a temperature above its freezing point
c. The combustion of gasoline
d. A ball thrown into the air
e. A raindrop falling to the ground
f. Iron rusting in a moist atmosphere

S16.1.2

spontaneous; nonspontaneous; spontaneous; nonspontaneous; spontaneous; spontaneous

Q16.1.4

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

Q16.1.5

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

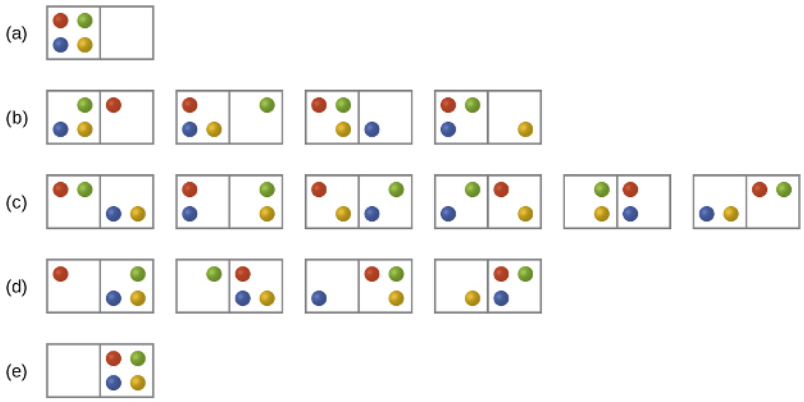
S16.1.5

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

16.2: Entropy Exercises

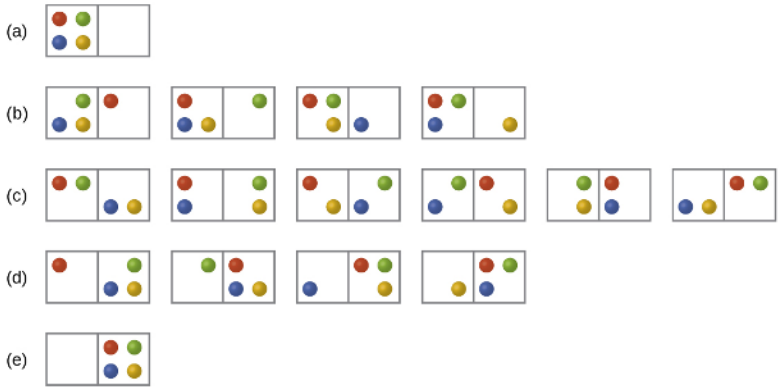
Q16.2.1

In the below Figure all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).



Q16.2.2

In Figure all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution to distribution (d).



S16.2.2

There are four initial microstates and four final microstates.

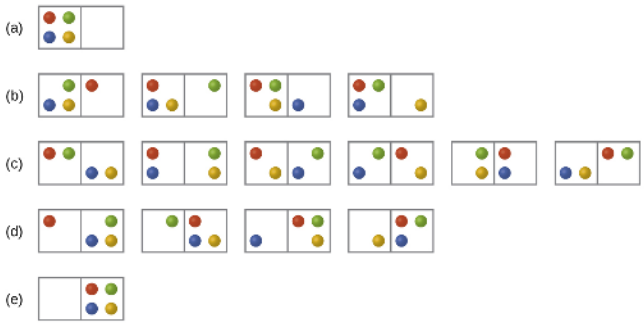
$$\Delta S = k \ln \frac{W_\mathrm{f}}{W_\mathrm{i}} = 1.38 \times 10^{-23}\ \mathrm{J/K} \times \ln \frac{4}{4} = 0 \tag{6.E.1}$$

Q16.2.3

How does the process described in the previous item relate to the system shown in [link]?

Q16.2.4

Consider a system similar to the one below, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

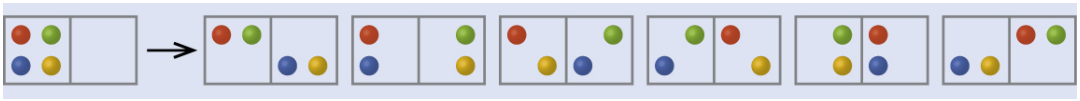


S16.2.4

The probability for all the particles to be on one side is $\frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

Q16.2.5

Consider the system shown in Figure. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?



Q16.2.6

Consider the system shown in Figure. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

S16.2.6

There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$$\Delta S = k \ln \left(\frac{W_f}{W_i} \right) = 1.38 \times 10^{-23} \text{ J/K} \times \ln \left(\frac{4}{1} \right) = 1.91 \times 10^{-23} \text{ J/K} \tag{6.E.2}$$

Q16.2.7

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

a. $H_2(g)$, $HBrO_4(g)$, $HBr(g)$
b. $H_2O(l)$, $H_2O(g)$, $H_2O(s)$
c. $He(g)$, $Cl_2(g)$, $P_4(g)$

Q16.2.8

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

S16.2.8

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

Q16.2.9

Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$$\mathrm{I_2}(s) \longrightarrow \mathrm{I_2}(g) \tag{6.E.3}$$

$$\mathrm{I_2}(s) \longrightarrow \mathrm{I_2}(l) \tag{6.E.4}$$

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

Q16.2.11

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

a. $C_2H_5OH(l)$ or $C_3H_7OH(l)$
b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
c. 2Hor $H(g)$

S16.2.11

$C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. $C_2H_5OH(g)$ as it is in the gaseous state. $2H(g)$, since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

Q16.2.11

Predict the sign of the entropy change for the following processes:

a. An ice cube is warmed to near its melting point.
b. Exhaled breath forms fog on a cold morning.
c. Snow melts.

Q16.2.12

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

a. $\mathrm{Pb^{2+}}(aq) + \mathrm{S^{2-}}(aq) \longrightarrow \mathrm{PbS}(s)$
b. $2\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$
c. $2\,\mathrm{C_6H_{14}}(l) + 19\,\mathrm{O_2}(g) \longrightarrow 14\,\mathrm{H_2O}(g) + 12\,\mathrm{CO_2}(g)$

S16.2.12

Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. Negative. There is a net loss of three moles of gas from reactants to products. Positive. There is a net increase of seven moles of gas from reactants to products.

Q16.2.13

Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

Q16.2.14

Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

S16.2.14

$$\mathrm{C_6H_6}(l) + 7.5\mathrm{O_2}(g) \longrightarrow 3\,\mathrm{H_2O}(g) + 6\,\mathrm{CO_2}(g) \tag{6.E.5}$$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

16.3: The Second and Third law

Q16.3.0

What is the difference between ΔS, $\Delta S°$, and ΔS°_{298} for a chemical change?

Q16.3.1

Calculate ΔS°_{298} for the following changes.

a. $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(g)$
b. $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l)$
c. $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}(g)$
d. $\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$
e. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l)$
f. $2\,\mathrm{HCl}(g) + \mathrm{Pb}(s) \longrightarrow \mathrm{PbCl_2}(s) + \mathrm{H_2}(g)$
g. $\mathrm{Zn}(s) + \mathrm{CuSO_4}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(s)$

S16.3.1

107 J/K; −86.4 J/K; 133.2 J/K; 118.8 J/K; −326.6 J/K; −171.9 J/K; (g) −7.2 J/K

Q16.3.2

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under standard state conditions to give gaseous carbon dioxide and liquid water.

Q16.3.3

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under standard state conditions to give gaseous carbon dioxide and water.

S16.3.3

100.6 J/K

Q16.3.4

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is:

$$\mathrm{Fe_2O_3}(s) + 2\,\mathrm{Al}(s) \longrightarrow \mathrm{Al_2O_3}(s) + 2\,\mathrm{Fe}(s) \tag{6.E.6}$$

Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

Q16.3.5

Using the relevant S°_{298} values listed in Appendix G, calculate S°_{298} for the following changes:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$
b. $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

S16.3.5

−198.1 J/K; −348.9 J/K

Q16.3.6

From the following information, determine ΔS°_{298} for the following:

a. $\mathrm{N}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) \quad \Delta S^\circ_{298} = ?$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta S^\circ_{298} = 24.8\ \mathrm{J/K}$
c. $\mathrm{N_2}(g) \longrightarrow 2\,\mathrm{N}(g) \quad \Delta S^\circ_{298} = 115.0\ \mathrm{J/K}$
d. $\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{O}(g) \quad \Delta S^\circ_{298} = 117.0\ \mathrm{J/K}$

Q16.3.7

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

\[S^\circ_{\ce{NaCl}(s)}=\mathrm{72.11\:\dfrac{J}{mol·K}}\hspace{40px} S^\circ_{\ce{NaCl}(l)}=\mathrm{95.06\:\dfrac{J}{mol·K}}\hspace{40px} \Delta H^\circ_\ce{fusion}=\mathrm{27.95\: kJ/mol}\]

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

S16.3.7

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

Q16.3.8

Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in [link]. All are run under standard state conditions and 25 °C.

Q16.3.8

2.86 J/K; 24.8 J/K; −113.2 J/K; −24.7 J/K; 15.5 J/K; 290.0 J/K

16.4: Free Energy

Q16.4.1

What is the difference between ΔG, $\Delta G°$, and ΔG°_{298} for a chemical change?

Q16.4.2

A reactions has ΔH°_{298} = 100 kJ/mol and $\Delta S^\circ_{298} = 250\ \text{J/mol·K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

S16.4.2

The reaction is nonspontaneous at room temperature. Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

Q16.4.3

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. $\ce{MnO2}(s) \longrightarrow \ce{Mn}(s) + \ce{O2}(g)$
b. $\ce{H2}(g) + \ce{Br2}(l) \longrightarrow 2\,\ce{HBr}(g)$
c. $\ce{Cu}(s) + \ce{S}(g) \longrightarrow \ce{CuS}(s)$
d. $2\,\ce{LiOH}(s) + \ce{CO2}(g) \longrightarrow \ce{Li2CO3}(s) + \ce{H2O}(g)$
e. $\ce{CH4}(g) + \ce{O2}(g) \longrightarrow \ce{C}(s,\ \text{graphite}) + 2\,\ce{H2O}(g)$
f. $\ce{CS2}(g) + 3\,\ce{Cl2}(g) \longrightarrow \ce{CCl4}(g) + \ce{S2Cl2}(g)$

S16.4.3

465.1 kJ nonspontaneous; −106.86 kJ spontaneous; −53.6 kJ spontaneous; −83.4 kJ spontaneous; −406.7 kJ spontaneous; −30.0 kJ spontaneous

Q16.4.4

Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. $\ce{C}(s,\ \text{graphite}) + \ce{O2}(g) \longrightarrow \ce{CO2}(g)$
b. $\ce{O2}(g) + \ce{N2}(g) \longrightarrow 2\,\ce{NO}(g)$
c. $2\,\ce{Cu}(s) + \ce{S}(g) \longrightarrow \ce{Cu2S}(s)$

d. $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$
e. $\mathrm{Fe_2O_3}(s) + 3\,\mathrm{CO}(g) \longrightarrow 2\,\mathrm{Fe}(s) + 3\,\mathrm{CO_2}(g)$
f. $\mathrm{CaSO_4 \cdot 2\,H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\,\mathrm{H_2O}(g)$

Given:

$$\mathrm{P_4}(s) + 5\,\mathrm{O_2}(g) \longrightarrow \mathrm{P_4O_{10}}(s) \quad \Delta G^\circ_{298} = -2697.0\ \mathrm{kJ/mol} \tag{6.E.7}$$

$$2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(g) \quad \Delta G^\circ_{298} = -457.18\ \mathrm{kJ/mol} \tag{6.E.8}$$

$$6\,\mathrm{H_2O}(g) + \mathrm{P_4O_{10}}(g) \longrightarrow 4\,\mathrm{H_3PO_4}(l) \quad \Delta G^\circ_{298} = -428.66\ \mathrm{kJ/mol} \tag{6.E.9}$$

Q16.4.5

a. Determine the standard free energy of formation, ΔG°_f, for phosphoric acid.
b. How does your calculated result compare to the value in Appendix G? Explain.

S16.4.5

−1124.3 kJ/mol for the standard free energy change. The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

Q16.4.6

Is the formation of ozone ($\mathrm{O_3}(g)$) from oxygen ($\mathrm{O_2}(g)$) spontaneous at room temperature under standard state conditions?

Q16.4.7

Consider the decomposition of red mercury(II) oxide under standard state conditions.

$$2\,\mathrm{HgO}(s,\ \mathrm{red}) \longrightarrow 2\,\mathrm{Hg}(l) + \mathrm{O_2}(g) \tag{6.E.10}$$

a. Is the decomposition spontaneous under standard state conditions?
b. Above what temperature does the reaction become spontaneous?

S16.4.7

The reaction is nonspontaneous; Above 566 °C the process is spontaneous.

Q16.4.8

Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

a. Ammonia: $2\,\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$
b. Diborane: $\mathrm{B_2H_6}(g) \longrightarrow 2\,\mathrm{B}(g) + 3\,\mathrm{H_2}(g)$
c. Hydrazine: $\mathrm{N_2H_4}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2}(g)$
d. Hydrogen peroxide: $\mathrm{H_2O_2}(l) \longrightarrow \mathrm{H_2O}(g) + \frac{1}{2}\mathrm{O_2}(g)$

Q16.4.9

Calculate ΔG° for each of the following reactions from the equilibrium constant at the temperature given.

a. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \mathrm{T} = 2000\ ^\circ\mathrm{C} \quad K_p = 4.1 \times 10^{-4}$
b. $\mathrm{H_2}(g) + \mathrm{I_2}(g) \longrightarrow 2\,\mathrm{HI}(g) \quad \mathrm{T} = 400\ ^\circ\mathrm{C} \quad K_p = 50.0$
c. $\mathrm{CO_2}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{CO}(g) + \mathrm{H_2O}(g) \quad \mathrm{T} = 980\ ^\circ\mathrm{C} \quad K_p = 1.67$
d. $\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g) \quad \mathrm{T} = 900\ ^\circ\mathrm{C} \quad K_p = 1.04$
e. $\mathrm{HF}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \quad \mathrm{T} = 25\ ^\circ\mathrm{C} \quad K_p = 7.2 \times 10^{-4}$
f. $\mathrm{AgBr}(s) \longrightarrow \mathrm{Ag^+}(aq) + \mathrm{Br^-}(aq) \quad \mathrm{T} = 25\ ^\circ\mathrm{C} \quad K_p = 3.3 \times 10^{-13}$

S16.4.9

1.5×10^2 kJ; −21.9 kJ; −5.34 kJ; −0.383 kJ; 18 kJ; 71 kJ

Q16.4.10

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. $Cl_2(g) + Br_2(g) \longrightarrow 2\,BrCl(g) \quad T = 25\ °C \quad K_p = 4.7 \times 10^{-2}$
b. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad T = 500\ °C \quad K_p = 48.2$
c. $H_2O(l) \rightleftharpoons H_2O(g) \quad T = 60\ °C \quad K_p = 0.196\ atm$
d. $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \quad T = 550\ °C \quad K_p = 4.90 \times 10^2$
e. $CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3^+(aq) + OH^-(aq) \quad T = 25\ °C \quad K_p = 4.4 \times 10^{-4}$
f. $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2\,I^-(aq) \quad T = 25\ °C \quad K_p = 8.7 \times 10^{-9}$

Q16.4.11

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a. $O_2(g) + 2\,F_2(g) \longrightarrow 2\,OF_2(g) \quad \Delta G° = -9.2\ kJ$
b. $I_2(s) + Br_2(l) \longrightarrow 2\,IBr(g) \quad \Delta G° = 7.3\ kJ$
c. $2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \quad \Delta G° = -79\ kJ$
d. $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \quad \Delta G° = -1.6\ kJ$
e. $SnCl_4(l) \longrightarrow SnCl_4(l) \quad \Delta G° = 8.0\ kJ$

S16.4.11

$K = 41$; $K = 0.053$; $K = 6.9 \times 10^{13}$; $K = 1.9$; $K = 0.04$

Q16.4.2

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

a. $I_2(s) + Cl_2(g) \longrightarrow 2\,ICl(g) \quad \Delta G° = -10.88\ kJ$
b. $H_2(g) + I_2(s) \longrightarrow 2\,HI(g) \quad \Delta G° = 3.4\ kJ$
c. $CS_2(g) + 3\,Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \quad \Delta G° = -39\ kJ$
d. $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \quad \Delta G° = -141.82\ kJ$
e. $CS_2(g) \longrightarrow CS_2(l) \quad \Delta G° = -1.88\ kJ$

Q16.4.13

Calculate the equilibrium constant at the temperature given.

a. (a) $O_2(g) + 2\,F_2(g) \longrightarrow 2\,F_2O(g) \quad (T = 100\ °C)$
b. $I_2(s) + Br_2(l) \longrightarrow 2\,IBr(g) \quad (T = 0.0\ °C)$
c. $2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \quad (T = 575\ °C)$
d. $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \quad (T = -10.0\ °C)$
e. $SnCl_4(l) \longrightarrow SnCl_4(g) \quad (T = 200\ °C)$

S16.4.13

In each of the following, the value of ΔG is not given at the temperature of the reaction. Therefore, we must calculate $\Delta G°$ from the values $\Delta H°$ and $\Delta S°$ and then calculate ΔG from the relation $\Delta G° = \Delta H° - T\Delta S°$.

a. $K = 1.29$
b. $K = 2.51 \times 10^{-3}$
c. $K = 4.83 \times 10^3$
d. $K = 0.219$
e. $K = 16.1$

Q16.4.14

Calculate the equilibrium constant at the temperature given.

a. (a) $\mathrm{I_2}(s) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{ICl}(g) \quad (\mathrm{T} = 100\ ^\circ\mathrm{C})$
b. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \longrightarrow 2\,\mathrm{HI}(g) \quad (\mathrm{T} = 0.0\ ^\circ\mathrm{C})$
c. $\mathrm{CS_2}(g) + 3\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g) \quad (\mathrm{T} = 125\ ^\circ\mathrm{C})$
d. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{SO_3}(g) \quad (\mathrm{T} = 675\ ^\circ\mathrm{C})$
e. $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l) \quad (\mathrm{T} = 90\ ^\circ\mathrm{C})$

Q16.4.15

Consider the following reaction at 298 K:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g) \quad K_P = 0.142 \tag{6.E.11}$$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

S16.4.16

The standard free energy change is $\Delta G^\circ_{298} = -RT\ln K = 4.84\ \mathrm{kJ/mol}$. When reactants and products are in their standard states (1 bar or 1 atm), Q = 1. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): $Q < 1$, and ΔG_{298} becomes less positive as it approaches zero. At equilibrium, $Q = K$, and $\Delta G = 0$.

Q16.4.17

Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

Q16.4.18

Under what conditions is $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g)$ spontaneous?

S16.4.18

The reaction will be spontaneous at temperatures greater than 287 K.

Q16.4.19

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

Q16.4.20

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\,\mathrm{H_2S}(g) + \mathrm{SO_2}(g) \rightleftharpoons \frac{3}{8}\mathrm{S_8}(s,\ \text{rhombic}) + 2\,\mathrm{H_2O}(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

S16.4.20

$K = 5.35 \times 10^{15}$

The process is exothermic.

Q16.4.21

Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

Q16.4.22

In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

S16.4.22

1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

Q16.4.23

Benzene can be prepared from acetylene. $\mathbf{3\,C_2H_2}(g) \rightleftharpoons \mathbf{C_6H_6}(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

Q16.4.24

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

$$x = 1.29 \times 10^{-5}\ \text{atm} = P_{\mathrm{O_2}} \tag{6.E.12}$$

Q16.4.25

Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

$$\mathbf{CH_4}(g) + \mathbf{4\,Cl_2}(g) \longrightarrow \mathbf{CCl_4}(g) + \mathbf{4\,HCl}(g) \tag{6.E.13}$$

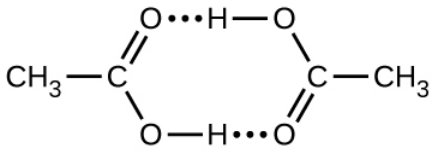
What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

Q16.4.25B

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

$$\mathbf{2\,CH_3CO_2H}(g) \longrightarrow \mathbf{(CH_3CO_2H)_2}(g) \tag{6.E.14}$$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

S16.4.25B

−0.16 kJ

Q16.4.26

Nitric acid, HNO_3, can be prepared by the following sequence of reactions:

$$\mathbf{4\,NH_3}(g) + \mathbf{5\,O_2}(g) \longrightarrow \mathbf{4\,NO}(g) + \mathbf{6\,H_2O}(g) \tag{6.E.15}$$

$$\mathbf{2\,NO}(g) + \mathbf{O_2}(g) \longrightarrow \mathbf{2\,NO_2}(g) \tag{6.E.16}$$

$$\mathbf{3\,NO_2}(g) + \mathbf{H_2O}(l) \longrightarrow \mathbf{2\,HNO_3}(l) + \mathbf{NO}(g) \tag{6.E.17}$$

How much heat is evolved when 1 mol of $NH_3(g)$ is converted to $HNO_3(l)$? Assume standard states at 25 °C.

Q16.4.27A

Determine ΔG for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$$\mathrm{SbCl_5}(g) \longrightarrow \mathrm{SbCl_3}(g) + \mathrm{Cl_2}(g) \tag{6.E.18}$$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

Chlorine molecules dissociate according to this reaction:

$$\mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{Cl}(g) \tag{6.E.19}$$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

S16.4.27A

a. (a) −22.1 kJ;
b. 61.6 kJ/mol

Q16.4.27

Given that the ΔG_f° for $Pb^{2+}(aq)$ and $Cl^-(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

Q16.4.28

Determine the standard free energy change, ΔG_f°, for the formation of $S^{2-}(aq)$ given that the ΔG_f° for $Ag^+(aq)$ and $Ag_2S(s)$ are 77.1 k/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

S16.4.28

90 kJ/mol

Q16.4.29

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Q16.4.30

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad \Delta G^\circ_{298} = 8.58\ \mathrm{kJ} \tag{6.E.20}$$

a. (a) Is the evaporation of water under standard thermodynamic conditions spontaneous?
b. Determine the equilibrium constant, K_P, for this physical process.
c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, P_{H_2O}, is 0.011 atm.
d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of P_{H_2O} in the air?

S16.4.30

(a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; K_p = 0.031; The evaporation of water is spontaneous; P_{H_2O} must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

Q16.4.31

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$$\mathrm{Glu} + \mathrm{ATP} \longrightarrow \mathrm{G6P} + \mathrm{ADP} \quad \Delta G^\circ_{298} = -17\ \mathrm{kJ} \tag{6.E.21}$$

In this process, ATP becomes ADP summarized by the following equation:

$$\mathrm{ATP} \longrightarrow \mathrm{ADP} \quad \Delta G^\circ_{298} = -30\ \mathrm{kJ} \tag{6.E.22}$$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$$\mathrm{Glu} \longrightarrow \mathrm{G6P} \quad \Delta G^\circ_{298} = ? \tag{6.E.23}$$

Q16.4.32

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$$\mathrm{G6P} \rightleftharpoons \mathrm{F6P} \quad \Delta G^\circ_{298} = 1.7\ \mathrm{kJ} \tag{6.E.24}$$

a. (a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

S16.4.32

(a) Nonspontaneous as $\Delta G^\circ_{298} > 0$; $\Delta G^\circ_{298} = -RT \ln K$, $\Delta G = 1.7 \times 10^3 + \left(8.314 \times 335 \times \ln \frac{28}{128}\right) = -2.5\ \mathrm{kJ}$. The forward reaction to produce F6P is spontaneous under these conditions.

Q16.4.33

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

a. (a) $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$
b. $\mathrm{HCl}(g) + \mathrm{NH_3}(g) \longrightarrow \mathrm{NH_4Cl}(s)$
c. $(\mathrm{NH_4})_2\mathrm{Cr_2O_7}(s) \longrightarrow \mathrm{Cr_2O_3}(s) + 4\,\mathrm{H_2O}(g) + \mathrm{N_2}(g)$
d. $2\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

S16.4.33

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

Q16.4.34

An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

$$\mathrm{Cu_2S}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{S}(s) \tag{6.E.25}$$

a. (a) Determine ΔG°_{298} for the decomposition of $Cu_2S(s)$.
b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG°_{298} for the process.
c. The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

Q16.4.35

What happens to ΔG°_{298} (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

a. (a) $\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$
b. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_3}(g)$
c. $\mathrm{HgO}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{O_2}(g)$

S16.4.35

a. (a) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG°_{298} therefore becomes more negative.
b. Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG°_{298} therefore becomes more negative.
c. Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium the reactants, which decreases the value of K. ΔG°_{298} therefore becomes more positive.

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CHAPTER OVERVIEW

7: Appendices

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General Chemistry

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7.5: Ionization Constants of Weak Acids
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7.7: Solubility Products
7.8: Standard Electrode (Half-Cell) Potentials
7.9: Standard Thermodynamic Properties for Selected Substances
7.10: The Periodic Table
7.11: Units and Conversion Factors
7.12: Water Properties

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7.1: Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases			
Acid or Base[1]	Density (g/mL)[2]	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia[3]	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Footnotes

1. 1 Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.
2. 2 This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.
3. 3 This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.

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7.2: Essential Mathematics

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$1000 = 1 \times 10^3$$
$$100 = 1 \times 10^2$$
$$10 = 1 \times 10^1$$
$$1 = 1 \times 10^0$$
$$0.1 = 1 \times 10^{-1}$$
$$0.001 = 1 \times 10^{-3}$$
$$2386 = 2.386 \times 1000 = 2.386 \times 10^3$$
$$0.123 = 1.23 \times 0.1 = 1.23 \times 10^{-1}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, 1,230,000,000 = 1.23×10^9, and 0.00000000036 = 3.6×10^{-10}.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 7.2.1: Adding Exponentials

Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

$$3.00 \times 10^{-3} = 300 \times 10^{-5}$$
$$(5.00 \times 10^{-5}) + (300 \times 10^{-5}) = 305 \times 10^{-5} = 3.05 \times 10^{-3}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Exercise 7.2.2: Subtracting Exponentials

Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6}$$
$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Exercise 7.2.3: Multiplying Exponentials

Multiply 4.2×10^{-8} by 2.0×10^3.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^3) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Exercise 7.2.4: Dividing Exponentials

Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Exercise 7.2.5: Squaring Exponentials

Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^2 = 4 \times 4 \times 10^{2\times(-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Exercise 7.2.6: Cubing Exponentials

Cube the number 2×10^{4}.

Solution

$$(2 \times 10^{4})^3 = 2 \times 2 \times 2 \times 10^{3\times4} = 8 \times 10^{12}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Exercise 7.2.7: Finding the Square Root of Exponentials

Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the

computation (indicated by underscoring in the following example).

Exercise 7.2.8: Addition and Subtraction with Significant Figures

Add 4.383 g and 0.0023 g.

Solution

$$\begin{array}{r} 4.38\underline{3}\ \text{g} \\ +\ 0.00\underline{23}\ \text{g} \\ \hline 4.38\underline{5}\ \text{g} \end{array}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Exercise 7.2.9: Multiplication and Division with Significant Figures

Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \times 6.\underline{6} = 4.\underline{1}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	−1
0.001	10^{-3}	−3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is −1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers. \[\log xy= \log x + \log y, \textrm{ and }\ln xy=\ln x + \ln y \nonumber \]
2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers. \[\log\dfrac{x}{y}=\log x-\log y,\textrm{ and } \ln\dfrac{x}{y}=\ln x-\ln y \nonumber \]
3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.

$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solving Quadratic Equations Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x*-*y*) Graphing

The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

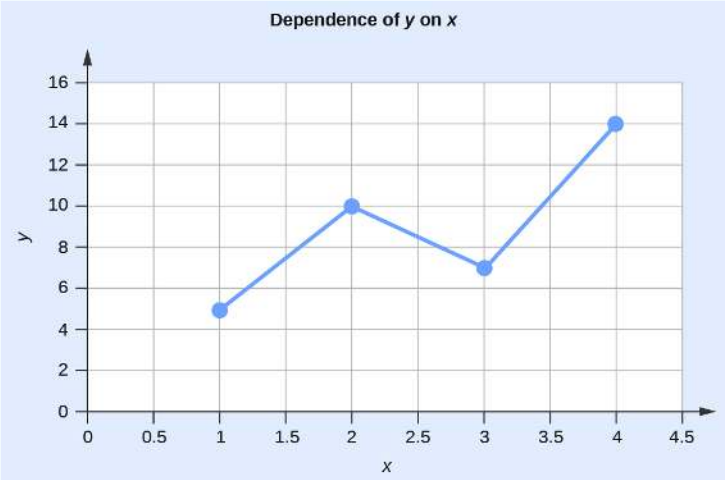
Exercise 7.2.10

Graphing the Dependence of y on x

Table for Exercise 10

x	y
1	5
2	10
3	7
4	14

This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x.



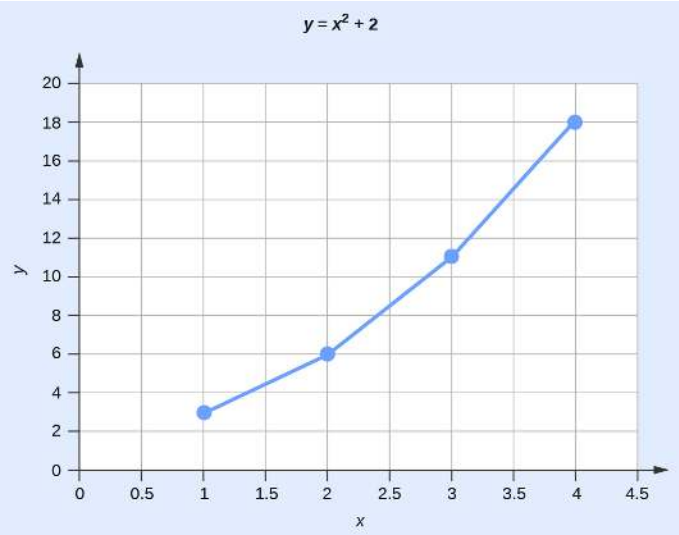
If the function that describes the dependence of y on x is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Exercise 7.2.11

Plotting Data Pairs If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

Table for Exercise 11

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



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7.3: Formation Constants for Complex Ions

Formation Constants for Complex Ions

Formation Constants for Complex Ions	
Equilibrium	K_f
$Al^{3+} + 6\,F^- \rightleftharpoons [AlF_6]^{3-}$	7×10^{19}
$Cd^{2+} + 4\,NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Cd^{2+} + 4\,CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	3×10^{18}
$Co^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^{5}
$Co^{3+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3×10^{33}
$Cu^{+} + 2\,CN \rightleftharpoons [Cu(CN)_2]^-$	1.0×10^{16}
$Cu^{2+} + 4\,NH_3 \overset{Cu(NH_3)_4}{\rightleftharpoons} {}^{2}+$	1.7×10^{13}
$Fe^{2+} + 6\,CN^- \overset{Fe(CN)_6}{\rightleftharpoons} {}^{4-}$	1.5×10^{35}
$Fe^{3+} + 6\,CN^- \overset{Fe(CN)_6}{\rightleftharpoons} {}^{3-}$	2×10^{43}
$Fe^{3+} + 6\,SCN^- \overset{Fe(SCN)_6}{\rightleftharpoons} {}^{3-}$	3.2×10^{3}
$Hg^{2+} + 4\,Cl^- \overset{HgCl_4}{\rightleftharpoons} {}^{2-}$	1.1×10^{16}
$Ni^{2+} + 6\,NH_3 \overset{Ni(NH_3)_6}{\rightleftharpoons} {}^{2}+$	2.0×10^{8}
$Ag^{+} + 2\,Cl^- \overset{AgCl_2}{\rightleftharpoons} -$	1.8×10^{5}
$Ag^{+} + 2\,CN^- \overset{Ag(CN)_2}{\rightleftharpoons} -$	1×10^{21}
$Ag^{+} + 2\,NH_3 \overset{Ag(NH_3)_2}{\rightleftharpoons} +$	1.7×10^{7}
$Zn^{2+} + 4\,CN^- \overset{Zn(CN)_4}{\rightleftharpoons} {}^{2-}$	2.1×10^{19}
$Zn^{2+} + 4\,OH^- \overset{Zn(OH)_4}{\rightleftharpoons} {}^{2-}$	2×10^{15}
$Fe^{3+} + SCN^- \overset{Fe(SCN)}{\rightleftharpoons} {}^{2}+$	8.9×10^{2}
$Ag^{+} + 4\,SCN^- \overset{Ag(SCN)_4}{\rightleftharpoons} {}^{3-}$	1.2×10^{10}
$Pb^{2+} + 4\,I^- \overset{PbI_4}{\rightleftharpoons} {}^{2-}$	3.0×10^{4}
$Pt^{2+} + 4\,Cl^- \overset{PtCl_4}{\rightleftharpoons} {}^{2-}$	1×10^{16}
$Cu^{2+} + 4\,CN \overset{Cu(CN)_4}{\rightleftharpoons} {}^{2-}$	1.0×10^{25}
$Co^{2+} + 4\,SCN^- \overset{Co(SCN)_4}{\rightleftharpoons} {}^{2-}$	1×10^{3}

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7.4: Fundamental Physical Constants

Fundamental Physical Constants

Fundamental Physical Constants	
Name and Symbol	Value
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217733 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg
Planck's constant (h)	$6.6260755 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

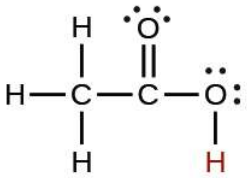
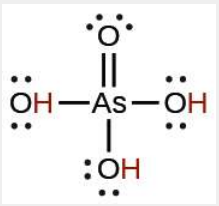
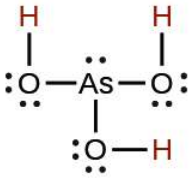
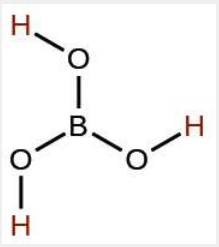
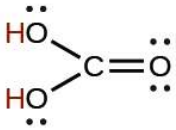
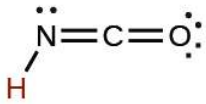
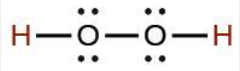
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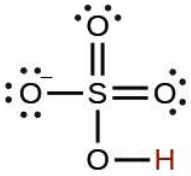
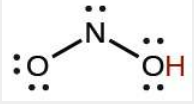
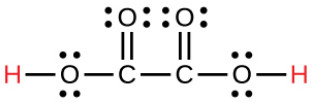
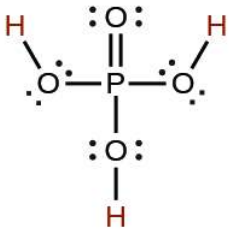
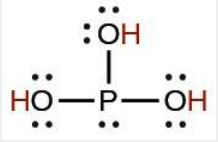
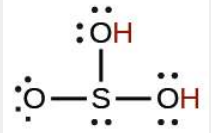
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7.5: Ionization Constants of Weak Acids

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}	

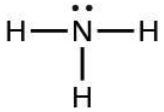
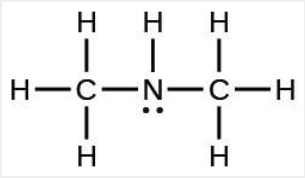
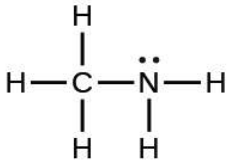
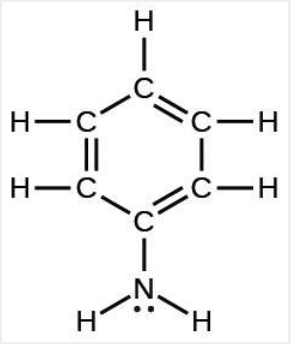
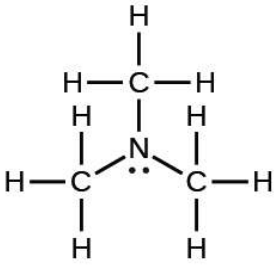
Ionization Constants of Weak Acids			
Acid	Formula	K_a at 25 °C	Lewis Structure
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	H_2S	8.9×10^{-8}	
	HS^-	1.0×10^{-19}	
hydrogen telluride	H_2Te	2.3×10^{-3}	
	HTe^-	1.6×10^{-11}	
hypobromous	HBrO	2.8×10^{-9}	
hypochlorous	HClO	2.9×10^{-8}	
nitrous	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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7.6: 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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7.7: Solubility Products

Solubility Products

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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}

Substance	K_{sp} at 25 °C
manganese	
$Mn(OH)_2$	2×10^{-13}
$MnCO_3$	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}

Substance	K_{sp} at 25 °C
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.2×10^{-5}
Ag_3PO_4	1.8×10^{-18}
strontium	
$Sr(OH)_2 \cdot 8H_2O$	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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7.8: 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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7.9: Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances

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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})
$Ba^{2+}(aq)$	-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			

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
$\mathbf{H^+}$ (aq)	0	0	0
$\mathbf{OH^-}$ (aq)	-230.0	-157.2	-10.75
$\mathbf{H_3O^+}$ (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
$\mathbf{I^-}$ (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
$\mathbf{Fe^{2+}}$ (aq)	-89.1	-78.90	-137.7
$\mathbf{Fe^{3+}}$ (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
$\mathbf{Pb^{2+}}$ $\mathbf{(aq)}$	-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
$\mathbf{Li^+}$ $\mathbf{(aq)}$	-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			
$\mathbf{Mg^{2+}}$ $\mathbf{(aq)}$	-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

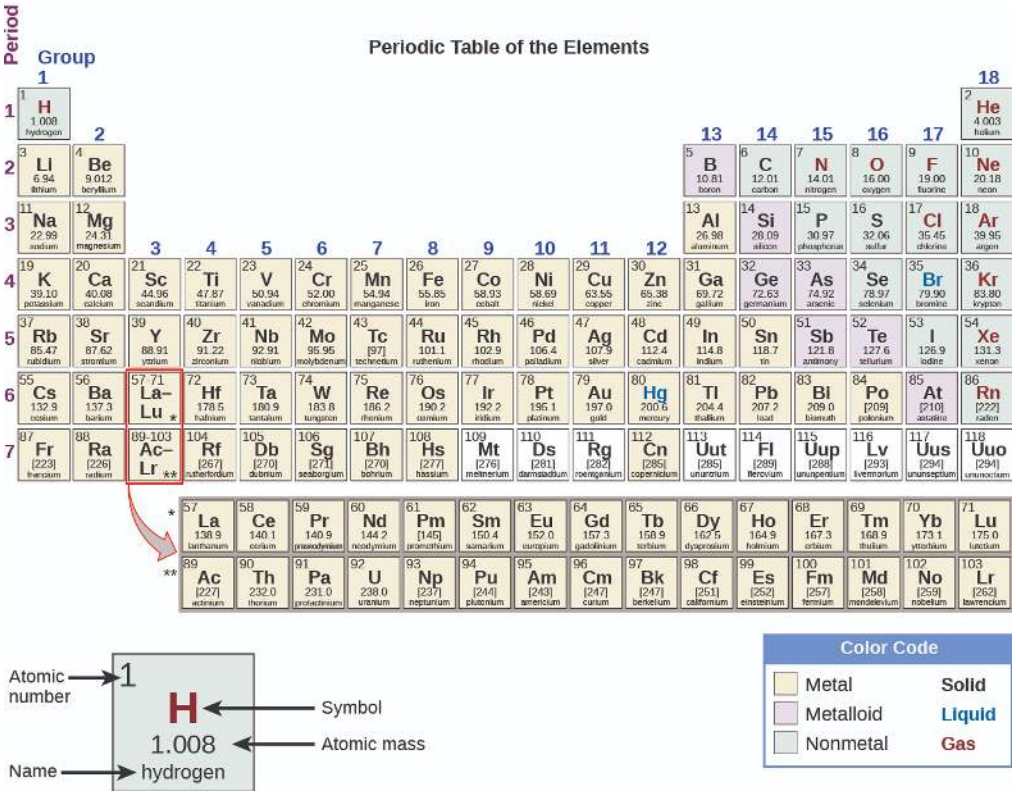
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
SnO(s)	–285.8	–256.9	56.5
SnO_2(s)	–577.6	–515.8	49.0
$SnCl_4$(l)	–511.3	–440.1	258.6
$SnCl_4$(g)	–471.5	–432.2	365.8
titanium			
Ti(s)	0	0	30.7
Ti(g)	473.0	428.4	180.3
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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7.10: The Periodic Table



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7.11: Units and Conversion Factors

Units of Length

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume

Units of Volume			
liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts	liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)	dry quart	= 1.1012 L
microliter (μL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)	cubic foot (US)	= 28.316 L

Units of Mass

Units of Mass			
gram (g)	= 0.001 kg (exact, definition)	ounce (oz) (avoirdupois)	= 28.35 g
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184×10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218×10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Units of Pressure

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

Footnotes

1. 1 BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

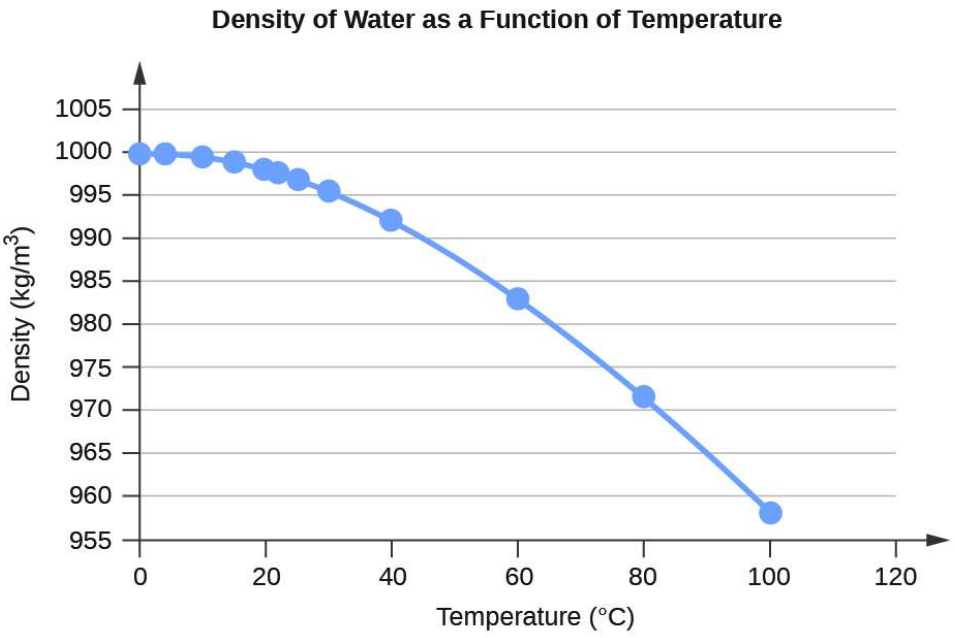
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7.12: Water Properties

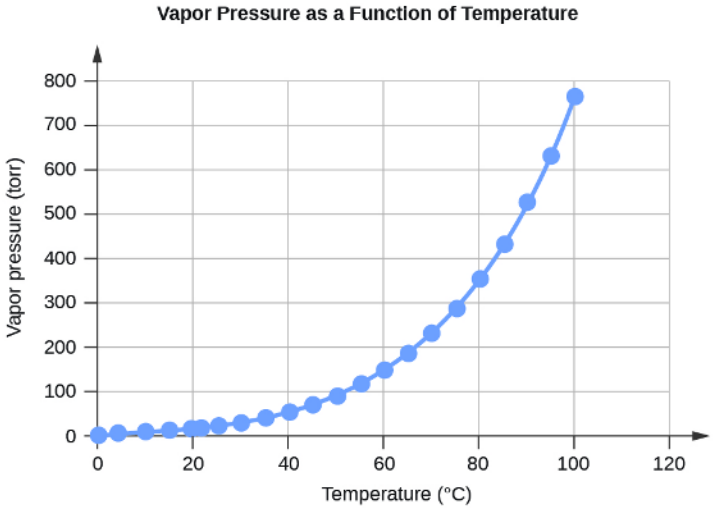
Water Density (kg/m3) at Different Temperatures (°C)

Temperature[1]	Density
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4



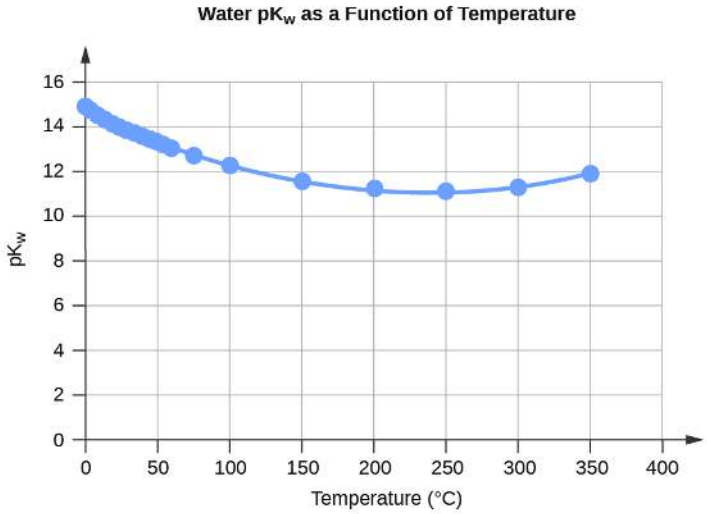
Water Vapor Pressure at Different Temperatures (°C)

Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522
20	17.5	2333.135
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7



Water Kw and pKw at Different Temperatures (°C)

Temperature	K_w 10^{-14}	pK_w[2]
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25



Specific Heat Capacity for Water

Specific Heat Capacity for Water
$C°(H_2O(l)) = 4184\ J{\cdot}K^{-1}{\cdot}kg^{-1} = 4.184\ J{\cdot}g^{-1}{\cdot}°C^{-1}$
$C°(H_2O(s)) = 1864\ J{\cdot}K^{-1}{\cdot}kg^{-1}$
$C°(H_2O(g)) = 2093\ J{\cdot}K^{-1}{\cdot}kg^{-1}$

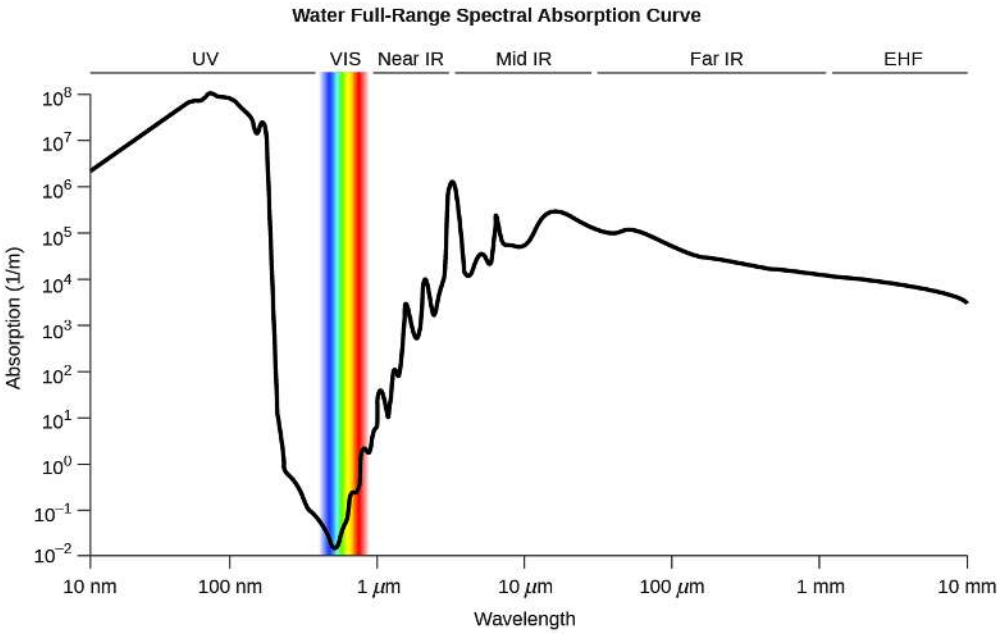
Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.088
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
$K_f = 1.86°C{\cdot}kg{\cdot}mol^{-1}$ (cryoscopic constant)
$K_b = 0.51°C{\cdot}kg{\cdot}mol^{-1}$ (ebullioscopic constant)

<figure class="ui-has-child-figcaption">



Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The y-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e (e = 2.718281828).

Footnotes

1. 1 Data for t < 0 °C are for supercooled water
2. 2 $pK_w = -\log_{10}(K_w)$

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