CHEM 1020: GENERAL CHEMISTRY II



S.N. Yasapala
Prince George's Community College

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Glossary

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Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Chemical Kinetics

Topic hierarchy

1.1: Prelude to Kinetics
1.2: Rate of a Chemical Reaction
1.3: Factors Affecting Reaction Rates
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1.5: Concentration and Rates (Differential Rate Laws)
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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.

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.2: Rate of a Chemical Reaction

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

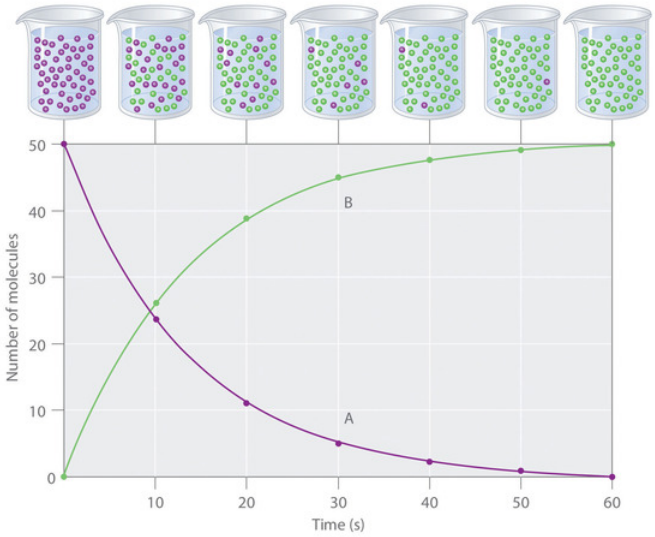


Figure **1.2.1**: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure **1.2.1**; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure **1.2.1**. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{1.2.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 1.2.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*



A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 1.2.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure **1.2.2**.

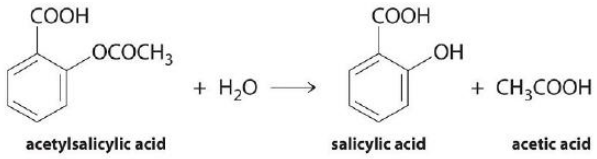


Figure **1.2.2**: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table **1.2.1** and are shown in the graph in Figure **1.2.3**.

Table **1.2.1**: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 1.2.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

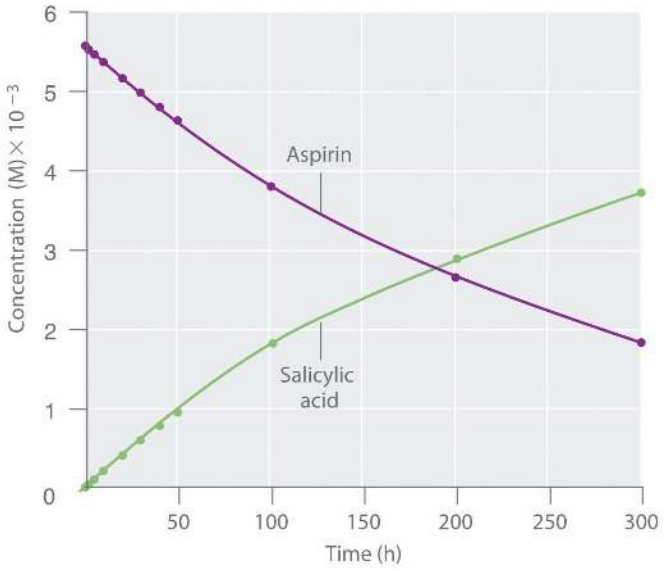


Figure 1.2.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2 \times 10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 1.2.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73 \times 10^{-3}\text{ M}) - (2.91 \times 10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2 \times 10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{1.2.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{1.2.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 1.2.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 1.2.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{1.2.4}$$

Example 1.2.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.

B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Exercise 1.2.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[SO_2]}{2\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*



Example 1.2.2: Decomposition Reaction II

Using the reaction shown in Example 1.2.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example **1.2.1**, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example **1.2.1**, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\text{ M} - 0.0388\text{ M}}{2(360\text{ s})} = 2.65 \times 10^{-5}\text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 1.2.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

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

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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.

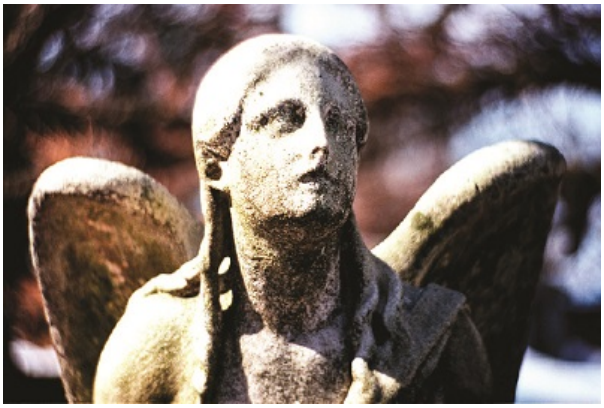


Figure **1.3.2**: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, 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.

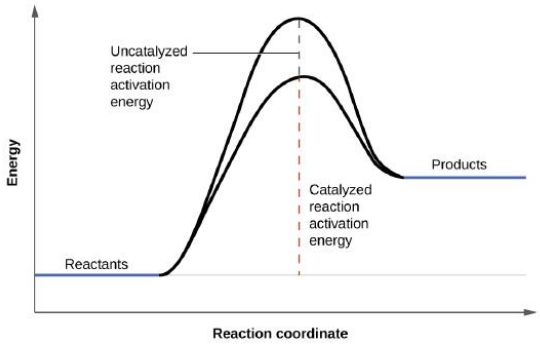


Figure **1.3.3**: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

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: Instantaneous Rate of a Chemical Reaction

Learning Objectives

- To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.

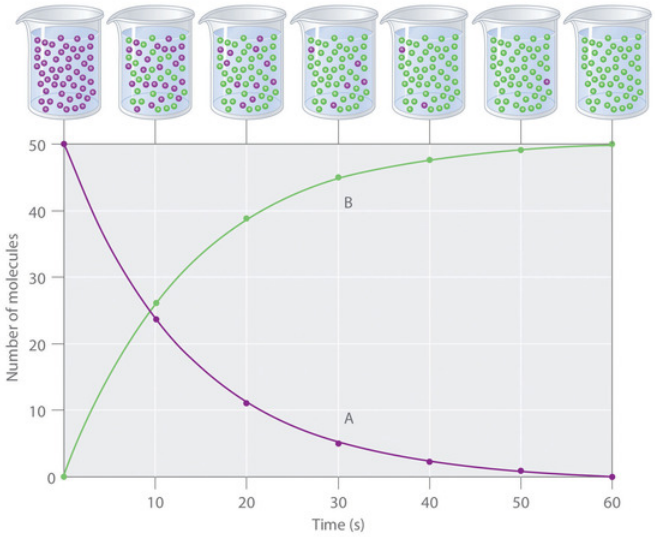


Figure 1.4.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 1.4.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 1.4.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{1.4.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means “change in.” Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 1.4.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*



A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 1.4.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure **1.4.2**.

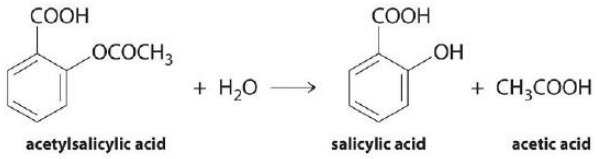


Figure **1.4.2**: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table **1.4.1** and are shown in the graph in Figure **1.4.3**.

Table **1.4.1**: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 1.4.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

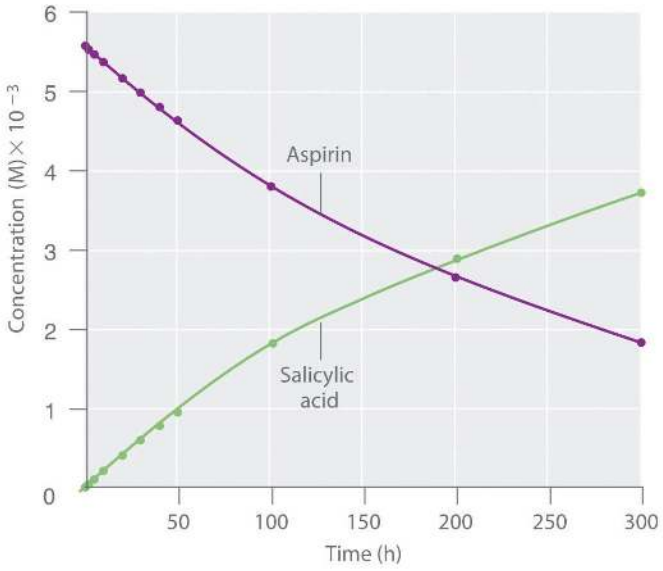


Figure 1.4.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= \frac{0.040 \times 10^{-3}\text{ M} - 0\text{ M}}{2.0\text{ h}} = 2.0 \times 10^{-5}\text{ M/h}\end{aligned}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\begin{aligned}\text{rate}_{(t=0-2.0\text{ h})} &= -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\text{ h} - 0\text{ h}} \\ &= -\frac{(5.51 \times 10^{-3}\text{ M}) - (5.55 \times 10^{-3}\text{ M})}{2.0\text{ h}} \\ &= 2 \times 10^{-5}\text{ M/h}\end{aligned}$$

If the reaction rate is calculated during the last interval given in Table 1.4.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\begin{aligned}\text{rate}_{(t=200-300\text{h})} &= \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\text{ h} - 200\text{ h}} \\ &= -\frac{(3.73 \times 10^{-3}\text{ M}) - (2.91 \times 10^{-3}\text{ M})}{100\text{ h}} \\ &= 8.2 \times 10^{-6}\text{ M/h}\end{aligned}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{1.4.2}$$

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{1.4.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 1.4.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 1.4.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{1.4.4}$$

Example 1.4.1: Decomposition Reaction I

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.

B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

? Exercise 1.4.1: Contact Process I

The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer

$$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[SO_2]}{2\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$

Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*



✓ Example 1.4.2: Decomposition Reaction II

Using the reaction shown in Example 1.4.1, calculate the reaction rate from the following data taken at 56°C:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

calculate the reaction rate from the following data taken at 56°C:

Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example **1.4.1**, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example **1.4.1**, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2(600\text{ s} - 240\text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197\text{ M} - 0.0388\text{ M}}{2(360\text{ s})} = 2.65 \times 10^{-5}\text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[NO_2]}{4\Delta t} = \frac{[NO_2]_{600} - [NO_2]_{240}}{4(600\text{ s} - 240\text{ s})} = \frac{0.0699\text{ M} - 0.0314\text{ M}}{4(360\text{ s})} = 2.67 \times 10^{-5}\text{ M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{[O_2]_{600} - [O_2]_{240}}{600\text{ s} - 240\text{ s}} = \frac{0.0175\text{ M} - 0.00792\text{ M}}{360\text{ s}} = 2.66 \times 10^{-5}\text{ M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 1.4.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

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

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1.5: Concentration and Rates (Differential Rate Laws)

Learning Objectives

- To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ([R]) after a given amount of time (t); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{1.5.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{1.5.2}$$

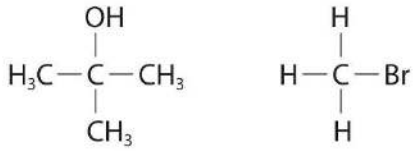
The proportionality constant (k) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of k, however, does not change as the reaction progresses under a given set of conditions.

> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers m and n, respectively. The values of m and n are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; m and n need not be integers. For example, Equation 1.5.2 tells us that Equation 1.5.1 is m^{th} order in reactant A and n^{th} order in reactant B. It is important to remember that n and m are not related to the stoichiometric coefficients a and b in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: $m + n$.

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone.



t-butanol methyl bromide

This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{1.5.3}$$

Combining the rate expression in Equation 1.5.2 with the definition of average reaction rate

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

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^m[\text{B}]^n \tag{1.5.4}$$

Inserting the identities of the reactants into Equation 1.5.4 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(\text{CH}_3)_3\text{CBr}]}{\Delta t} = k[(\text{CH}_3)_3\text{CBr}]^m[\text{H}_2\text{O}]^n \tag{1.5.5}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 1.5.4 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{1.5.6}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[\text{CH}_3\text{Br}]}{\Delta t} = k'[\text{CH}_3\text{Br}] \tag{1.5.7}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 1.5.7 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-]$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

Example 1.5.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

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

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:

$$\text{rate} = k[\mathrm{NO_2}]^m[\mathrm{CO}]^n$$

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:

$$\text{rate} = k[\mathrm{NO_2}]^2[\mathrm{CO}]^0 = k[\mathrm{NO_2}]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, 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 1.5.1A

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 1.5.1B

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

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

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

Example 1.5.2: Differential Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

a. $$2\text{HI}(g) \xrightarrow{\text{Pt}} \text{H}_2(g) + \text{I}_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\text{HI}]}{\Delta t}\right) = k[\text{HI}]^2$$

b. $$2\text{N}_2\text{O}(g) \xrightarrow{\Delta} 2\text{N}_2(g) + \text{O}_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\text{N}_2\text{O}]}{\Delta t}\right) = k$$

c. $$\text{cyclopropane}(g) \rightarrow \text{propane}(g)$$
$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$

Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A. Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

B. Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Add all exponents to obtain the overall reaction order.

C. Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution

1. **A** $[\text{HI}]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$k\text{M}^2 = \frac{\text{M}}{\text{s}}k = \frac{\text{M/s}}{\text{M}^2} = \frac{1}{\text{M}\cdot\text{s}} = \text{M}^{-1}\cdot\text{s}^{-1}$$

B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

C If the concentration of HI is doubled, the reaction rate will increase from $k[\text{HI}]_0^2$ to $k(2[\text{HI}])_0^2 = 4k[\text{HI}]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M\cdot s^{-1} = M/s$.

B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

? Exercise 1.5.2

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

a. $\mathrm{CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)} \quad \text{rate} = -\dfrac{\Delta[\mathrm{CH_3N{=}NCH_3}]}{\Delta t}$ (1.5.8)

$= k[\mathrm{CH_3N{=}NCH_3}]$ (1.5.9)

b. $\mathrm{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)} \quad \text{rate} = -\dfrac{\Delta[\mathrm{F_2}]}{\Delta t} = -\dfrac{1}{2}\left(\dfrac{\Delta[\mathrm{NO_2}]}{\Delta t}\right)$ (1.5.10)

$= k[\mathrm{NO_2}][\mathrm{F_2}]$ (1.5.11)

Answer a

s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.

Answer b

$M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow \textit{products}$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{1.5.12}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow \textit{products}$ are given in Table 1.5.1.

Table 1.5.1: Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow \textit{products}$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

The general rate law for the reaction is given in Equation 1.5.12. We can obtain m or n directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 1.5.3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\mathrm{A_1}]^m[\mathrm{B_1}]^n}{k[\mathrm{A_3}]^m[\mathrm{B_3}]^n}$$

Inserting the appropriate values from Table **1.5.3**,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{34 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[1.00\ \text{M}]^m[0.50\ \text{M}]^n}$$

Because 1.00 to any power is 1, $[1.00\ \text{M}]^m = 1.00\ \text{M}$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for m.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for n.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_5]^m[\text{B}_5]^n}$$

Substituting the appropriate values from Table **1.5.3**,

$$\frac{8.5 \times 10^{-3}\ \text{M/min}}{8.5 \times 10^{-3}\ \text{M/min}} = \frac{k[0.50\ \text{M}]^m[0.50\ \text{M}]^n}{k[0.50\ \text{M}]^m[1.00\ \text{M}]^n}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $\boldsymbol{n = 0}$; that is, the reaction is zeroth order in $\boldsymbol{B}$. The experimentally determined rate law is therefore

$$\text{rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table **1.5.3** into the experimentally determined rate law and solving for $\boldsymbol{k}$. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \text{M/min} = k(0.75\ \text{M})^2$$

$$3.4 \times 10^{-2}\ \text{M}^{-1}\cdot\text{min}^{-1} = \text{k}$$

You should verify that using data from any other row of Table **1.5.1** gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 1.5.3

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with $\boldsymbol{O_2}$ to give $\boldsymbol{NO_2}$, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{HNO}_2 + \text{HNO}_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Determine the rate law for the reaction and calculate the rate constant.

rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.

B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0125\ \text{M})} = 1.16 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{15.9 \times 10^{-3}\ \text{M/s}}{(0.0235\ \text{M})^2(0.0250\ \text{M})} = 1.15 \times 10^3\ \text{M}^{-2} \cdot \text{s}^{-1}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m + n) = 3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

? Exercise 1.5.3

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O^{2-}_{8(aq)} + 3I^-_{(aq)} \rightarrow 2SO^{2-}_{4(aq)} + I^-_{3(aq)}$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

kinetics data for this reaction at 25°C.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer:

rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ \text{M}^{-1}\cdot\text{s}^{-1}$



A Video Discussing Initial Rates and Rate Law Expressions. Video Link: Initial Rates and Rate Law Expressions(opens in new window) [youtu.be]

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

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1.6: Integrated Rate Laws (Zeroth, First, and second order reactions)

Learning Objectives

- To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{1.6.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.

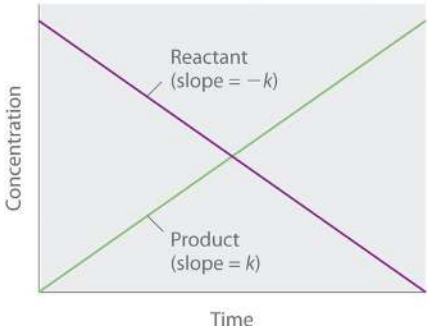


Figure 1.6.1: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{1.6.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation 1.6.2 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

Units

In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g) \tag{1.6.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{1.6.4}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure **1.6.2**, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.

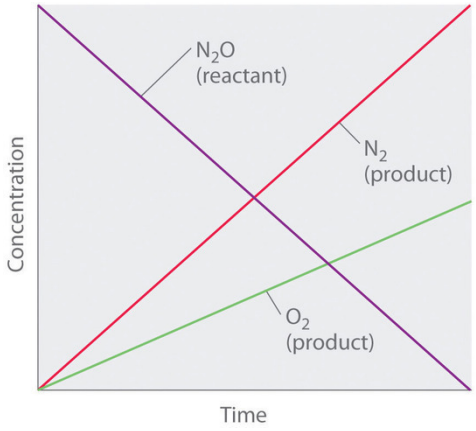


Figure **1.6.2**: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactiant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is



Figure **1.6.2**

where \ce{NAD^{+}\} (nicotinamide adenine dinucleotide) and **NADH** (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure **1.6.3*a***). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by

the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure **1.6.3**).

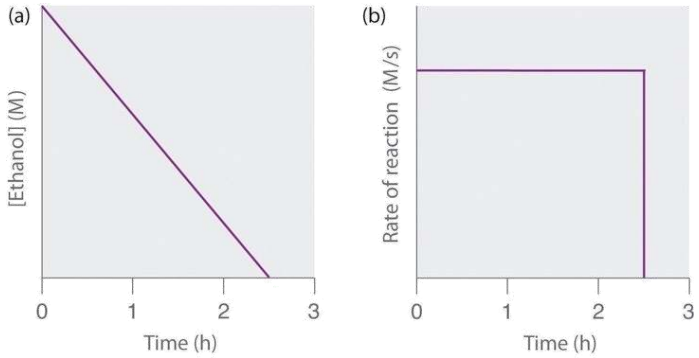


Figure **1.6.3**: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{1.6.5}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{1.6.6}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 1.6.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 1.6.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln[A]_0 - kt \tag{1.6.7}$$

Because Equation 1.6.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 1.6.5) or the integrated rate law (Equation 1.6.7) can be used to determine whether a particular reaction is first order.

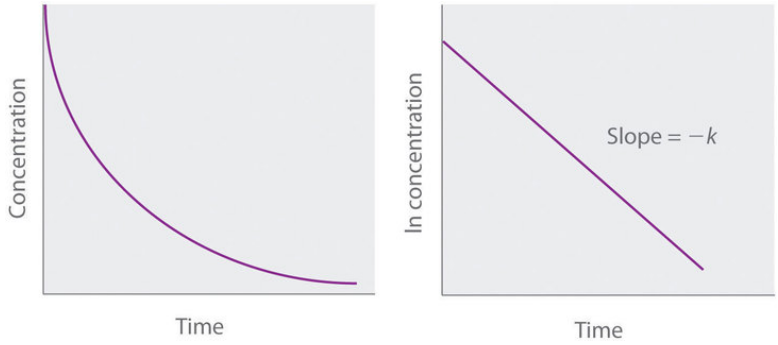


Figure **1.6.4**: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

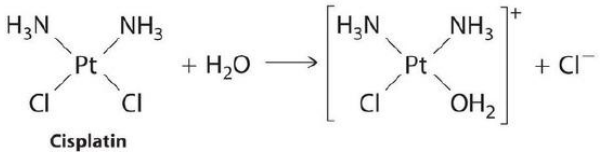


Figure **1.6.5**: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure **1.6.5** is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure **1.6.4** have been studied extensively to find ways of maximizing the concentration of the active species.

> *If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.*

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table **1.6.1**. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table **1.6.1**: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table **1.6.1** shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = $k[\text{cisplatin}]^1$. Thus the

reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table **1.6.1**. For example, substituting the values for Experiment 3 into Equation 1.6.5,

$$3.6 \times 10^{-5}\ \text{M/min} = k(0.024\ \text{M})$$

$$1.5 \times 10^{-3}\ \text{min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 1.6.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$\mathbf{CH_3CH_2Cl\,(g) \xrightarrow{\Delta} HCl\,(g) + C_2H_4\,(g)}$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[CH_3CH_2Cl]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8}\ \text{M/s} = k(0.010\ \text{M})$$

$$1.6 \times 10^{-6}\ \text{s}^{-1} = k$$

Exercise 1.6.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure **1.6.6***a* shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

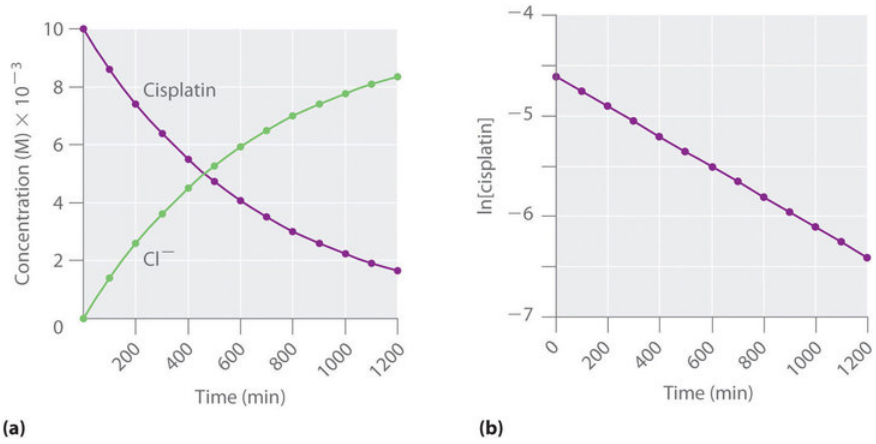


Figure **1.6.6**: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure **1.6.6**. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure **1.6.6** for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

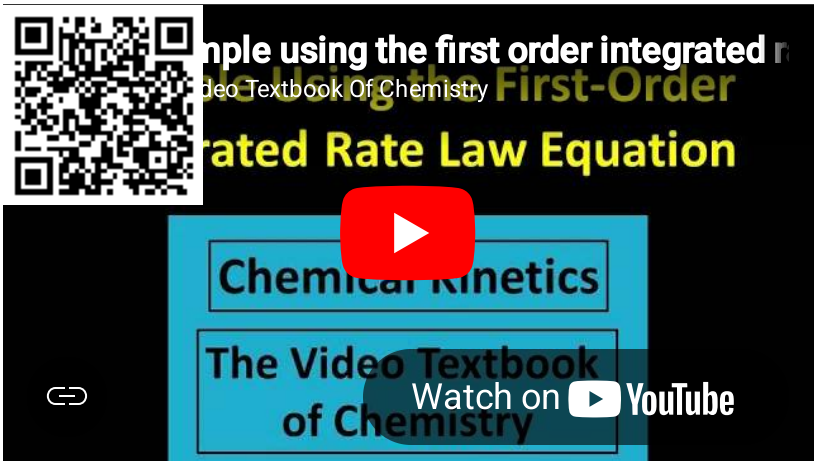
$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000\ \text{min} - 100\ \text{min}}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000\ \text{min} - 100\ \text{min}} = \frac{-6.12 - (-4.76)}{900\ \text{min}} = -1.51 \times 10^{-3}\ \text{min}^{-1}$$

$$k = 1.5 \times 10^{-3}\ \text{min}^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure **1.6.6** are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.



Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Example 1.6.2

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6}\ s^{-1}$) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.

B. Given a concentration [A], solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 1.6.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}\ s^{-1}$, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$\begin{aligned}[CH_3CH_2Cl]_{10\ h} &= [CH_3CH_2Cl]_0 e^{-kt} \\ &= 0.0200\ M(e^{-(1.6\times10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)]}) \\ &= 0.0189\ M\end{aligned}$$

We could also have used the logarithmic form of the integrated rate law (Equation 1.6.7):

$$\begin{aligned}\ln [CH_3CH_2Cl]_{10\ h} &= \ln [CH_3CH_2Cl]_0 - kt \\ &= \ln 0.0200 - (1.6 \times 10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)] \\ &= -3.912 - 0.0576 = -3.970 \\ [CH_3CH_2Cl]_{10\ h} &= e^{-3.970}\ M \\ &= 0.0189\ M\end{aligned}$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 1.6.7 gives the following:

$$\ln [CH_3CH_2Cl]_t = \ln [CH_3CH_2Cl]_0 - kt$$

$$kt = \ln [CH_3CH_2Cl]_0 - \ln [CH_3CH_2Cl]_t = \ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\left(\ln \frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}\right) = \frac{1}{1.6 \times 10^{-6}\ \text{s}^{-1}}\left(\ln \frac{0.0200\ \text{M}}{0.0050\ \text{M}}\right)$$

$$= \frac{\ln 4.0}{1.6 \times 10^{-6}\ \text{s}^{-1}} = 8.7 \times 10^5\ \text{s} = 240\ \text{h} = 2.4 \times 10^2\ \text{h}$$

? Exercise 1.6.2

In the exercise in Example **1.6.1**, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form

$$2\,A \longrightarrow \text{products}\cdot$$

A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\text{rate} = -\frac{\Delta[A]}{2\Delta t} = k[A]^2 \tag{1.6.8}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \tag{1.6.9}$$

Because Equation **1.6.9** has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of $1/[A]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

> *Second-order reactions generally have the form 2A → products or A + B → products.*



Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

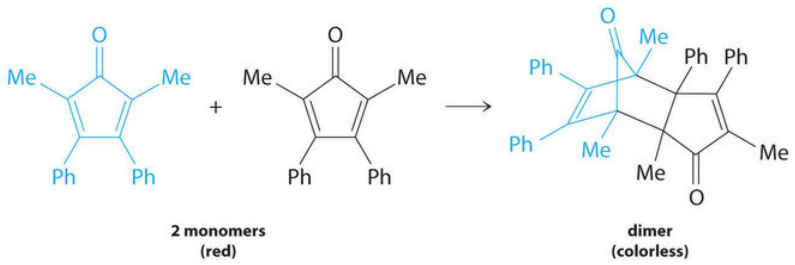


Figure **1.6.7**

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 1.6.8) or the integrated rate law (Equation 1.6.9).

Table **1.6.2**: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table **1.6.2**. From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ \text{M/min}}{1.8 \times 10^{-5}\ \text{M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3}\ \text{M}}{2.0 \times 10^{-3}\ \text{M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 1.6.8 and the data from any row in Table **1.6.2**, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{1.6.10}$$

$$8.0 \times 10^{-5}\ \text{M/min} = k(4.4 \times 10^{-3}\ \text{M})^2 \tag{1.6.11}$$

$$4.1\ \text{M}^{-1} \cdot \text{min}^{-1} = k \tag{1.6.12}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure **1.6.8***a*. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in Figure **1.6.8***b*. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1\ \text{M}^{-1}\cdot\text{min}^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.

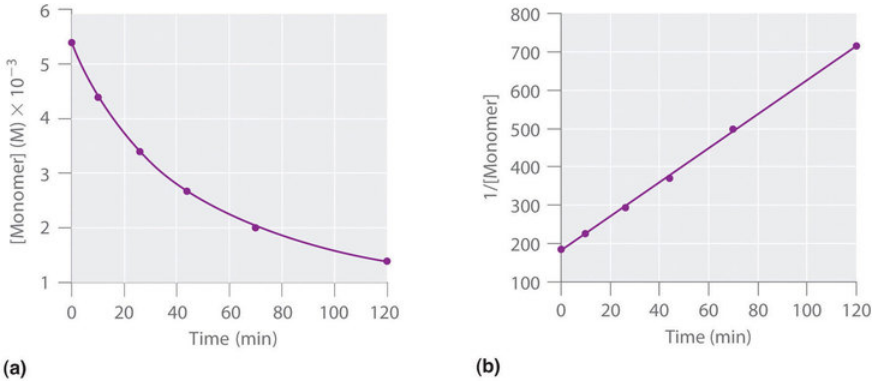


Figure **1.6.8**: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

✔ Example 1.6.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2\text{NO}_2(\text{g}) \xrightarrow{\Delta} 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\text{rate} = k[NO_2]^2$$
$$5.40 \times 10^{-5}\ \text{M/s} = k(0.010\ \text{M})^2$$
$$0.54\ \text{M}^{-1} \cdot \text{s}^{-1} = k$$

? Exercise 1.6.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO_2; $k = 1.4 \times 10^9\ M^{-1}\cdot s^{-1}$

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

Example 1.6.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 1.6.9) and the rate constant calculated above.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A. Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].
B. Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution

A We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 1.6.9,

$$\begin{aligned}\frac{1}{[NO_2]_{3600}} &= \frac{1}{[NO_2]_0} + kt \\ &= \frac{1}{0.056\ M} + [(0.54\ M^{-1}\cdot s^{-1})(3600\ s)] \\ &= 2.0 \times 10^3\ M^{-1}\end{aligned}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056$ M. To do this, we solve Equation 1.6.9 for t, using the concentrations given.

$$\begin{aligned}t &= \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k} \\ &= \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1}\cdot s^{-1}} \\ &= 3.0 \times 10^2\ s = 5.0\ min\end{aligned}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise 1.6.4

In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1}\cdot s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 1.6.9) and the rate constant calculated in the exercise in Example 1.6.3.

Answer

2.0×10^{-13} M; 6.4×10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this

reaction is as follows:

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

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

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

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

- **first-order reaction**:

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

$$[A] = [A]_0 e^{-kt}$$

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

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

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

1.6: Integrated Rate Laws (Zeroth, First, and second order reactions) is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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1.7: Half life

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 1.7.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2×10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2\,C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

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 1.7.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. 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:

$$\ln[A] = (-k)(t) + \ln [A]_0 \tag{1.7.1}$$

$$y = mx + b \tag{1.7.2}$$

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 1.7.2: 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 1.7.1.

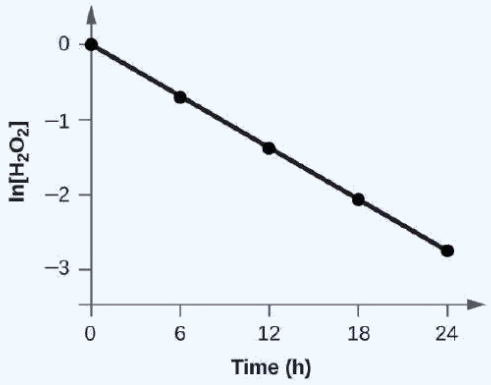


Figure 1.7.1: The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

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 1.7.2

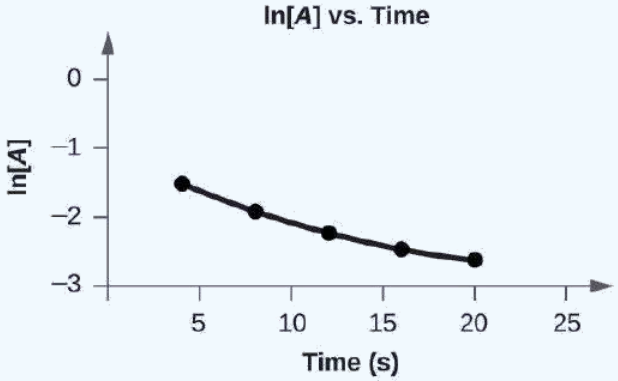
Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

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:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{1.7.3}$$

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

Example 1.7.3: 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 1.7.3

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 1.7.4: 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 **1.7.4**

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 ✔ **1.7.4**

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 **1.7.2**. 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.

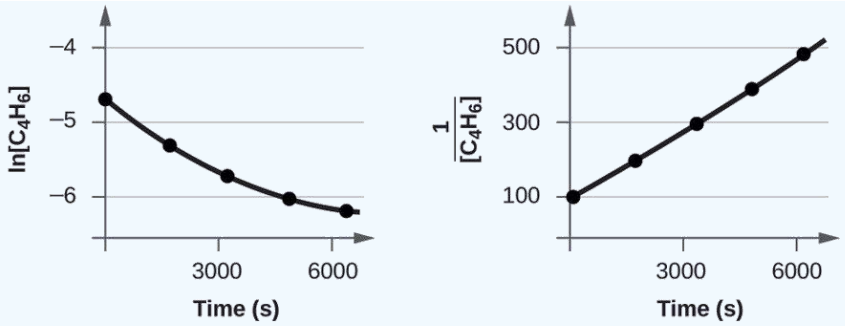


Figure **1.7.2**: These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

Exercise 1.7.4

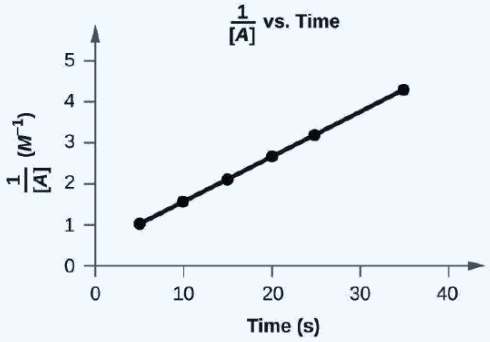
Does the following data fit a second-order rate law?

Data for second-order rate law

Trial	Time (s)	[*A*] (*M*)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer

Yes. The plot of $\frac{1}{[A]}$ vs. t is linear:



A graph, with the title “1 divided by [A] vs. Time” is shown, with the label, “Time (s),” on the x-axis. The label “1 divided by [A]” appears left of the y-axis. The x-axis shows markings beginning at zero and continuing at intervals of 10 up to and including 40. The y-axis on the left shows markings beginning at 0 and increasing by intervals of 1 up to and including 5. A line with an increasing trend is drawn through six points at approximately (4, 1), (10, 1.5), (15, 2.2), (20, 2.8), (26, 3.4), and (36, 4.4).

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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 **1.7.3** 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:

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

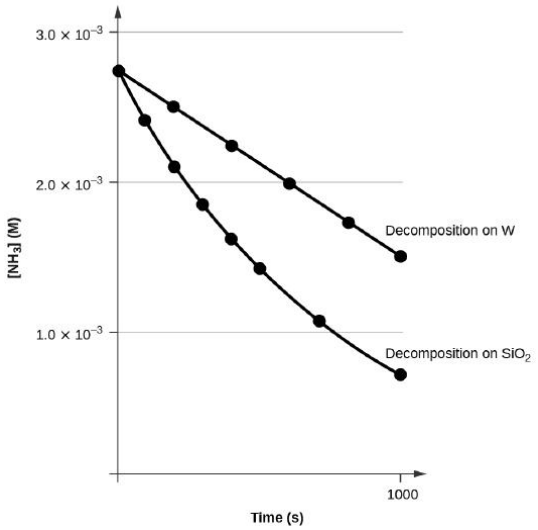


Figure **1.7.3**: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

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 1.7.5: 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 1.7.4.



Figure 1.7.4: 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 1.7.1

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

Answer

5.02 d.

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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 **1.7.1**.

Table 1.7.1: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	M s^{-1}	s^{-1}	M^{-1} s^{-1}
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ 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 1.7.1):

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

- integrated rate law for second-order reactions (Equation 1.7.3):

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

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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1.8: Collision Theory (Effect of temperature on a rate of a reaction)

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 **1.8.1**. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (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.

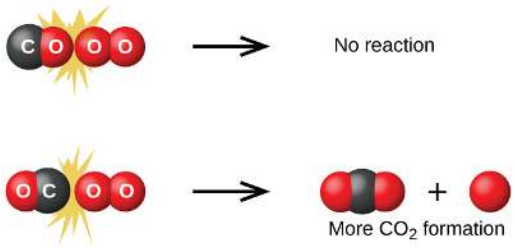


Figure **1.8.1**: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. 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 **1.8.2** 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.

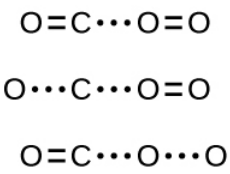


Figure **1.8.2**: Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first 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 **1.8.3** 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 **1.8.3**, 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:

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

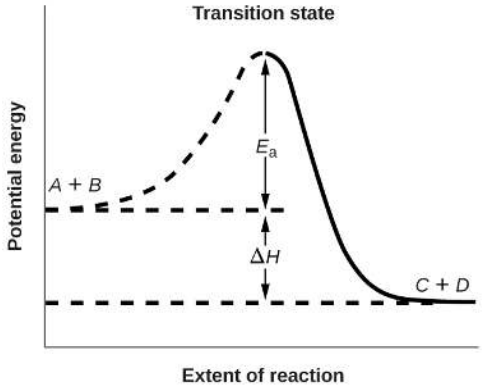


Figure **1.8.3**: This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of 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:

$$k = Ae^{-E_a/RT} \tag{1.8.1}$$

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 1.8.1) 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.

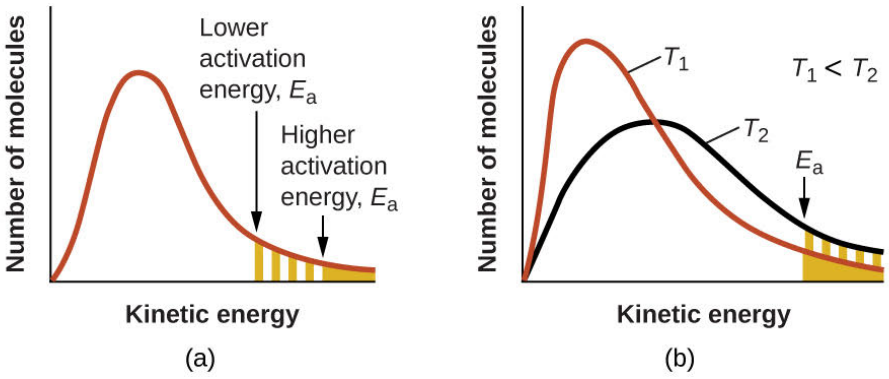


Figure 1.8.4: (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T2, more molecules have kinetic energies greater than Ea, as shown by the yellow shaded area.

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 1.8.4), 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 1.8.1

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

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

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 1.8.5 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.

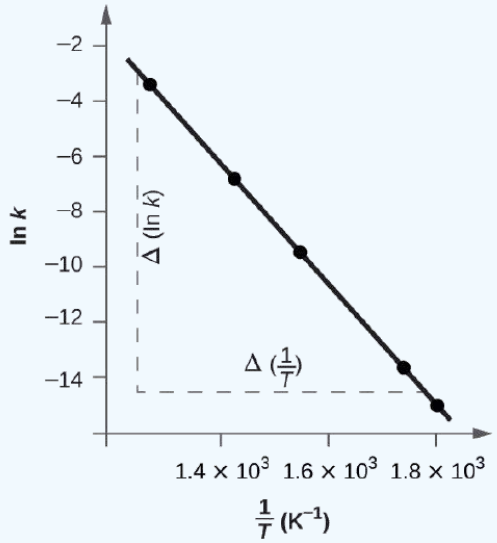


Figure 1.8.5: This graph shows the linear relationship between $\ln k$ and $\frac{1}{T}$ for the reaction $2\,HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

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 1.8.1

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

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

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

Answer

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.E: Kinetics (Practice Problems with Answers)

14.1: Factors that Affect Reaction Rates

Q14.1.1

What information can you obtain by studying the chemical kinetics of a reaction? Does a balanced chemical equation provide the same information? Why or why not?

S14.1.1

Kinetics gives information on the reaction rate and reaction mechanism; the balanced chemical equation gives only the stoichiometry of the reaction.

Q14.1.2

If you were tasked with determining whether to proceed with a particular reaction in an industrial facility, why would studying the chemical kinetics of the reaction be important to you?

S14.1.2

Studying chemical kinetics determines whether to proceed with a reaction as it measures the rate of a reaction. Reactions conducted in an industrial facility mix compounds together, heating and stirring them for a while, before moving to the next process. When the compounds are then moved to the next phase of the process it is important to know how long to hold the reaction at one stage before continuing, to make sure a reaction has finished before starting the next one

Q14.1.3

What is the relationship between each of the following factors and the reaction rate: reactant concentration, temperature of the reaction, physical properties of the reactants, physical and chemical properties of the solvent, and the presence of a catalyst?

S14.1.3

Reactant concentration:

Reaction rate and the concentration of reactants have a direct relationship; as concentration goes up, so does reaction rate. This is because a higher concentration causes the reactants to have a higher probability to collide with a another reactant particle, possibly inducing the chemical reaction. This comes from the Collision theory.

Reaction temperature:

Reaction rate and the reaction temperature also have a direct relationship; as temperature goes up, so does reaction rate. A higher temperature makes the particles move at a faster speed so when two or more reactant particles collide, they collide with more energy and are more likely to reach the activation energy threshold, starting a chemical reaction.

Physical properties of the reactants:

If the reactants have the same physical properties, they are more likely to react, increasing the reaction rate, because the reactants mix and are more likely to collide another one of the reactants.

Physical and chemical properties of the solvent:

The properties of the solvent also affect the rates of a reaction. High viscosity means that particles more slowly than in low viscosity solvents, so reaction rates are slower in high viscosity solvents than in low viscosity solvents. This indicates an inverse relationship between viscosity and reaction rate.

Presence of a catalyst:

The chemical definition of a catalyst in a substance that increases the rate of a reaction without being used up in the reaction. Therefore, if a catalyst is present, reaction rate increases.

Q14.1.4

A slurry is a mixture of a finely divided solid with a liquid in which it is only sparingly soluble. As you prepare a reaction, you notice that one of your reactants forms a slurry with the solvent, rather than a solution. What effect will this have on the reaction rate? What steps can you take to try to solve the problem?

Q14.1.5

Why does the reaction rate of virtually all reactions increase with an increase in temperature? If you were to make a glass of sweetened iced tea the old-fashioned way, by adding sugar and ice cubes to a glass of hot tea, which would you add first?

S14.1.5

Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. First dissolve sugar in the hot tea, and then add the ice.

Q14.1.6

In a typical laboratory setting, a reaction is carried out in a ventilated hood with air circulation provided by outside air. A student noticed that a reaction that gave a high yield of a product in the winter gave a low yield of that same product in the summer, even though his technique did not change and the reagents and concentrations used were identical. What is a plausible explanation for the different yields?

Q14.1.7

A very active area of chemical research involves the development of solubilized catalysts that are not made inactive during the reaction process. Such catalysts are expected to increase reaction rates significantly relative to the same reaction run in the presence of a heterogeneous catalyst. What is the reason for anticipating that the relative rate will increase?

Q14.1.8

Water has a dielectric constant more than two times greater than that of methanol (80.1 for H_2O and 33.0 for CH_3OH). Which would be your solvent of choice for a substitution reaction between an ionic compound and a polar reagent, both of which are soluble in either methanol or water? Why?

14.2: Reaction Rates

Q14.2.1

Explain why the reaction rate is generally fastest at early time intervals. For the second-order A + B → C, what would the plot of the concentration of C versus time look like during the course of the reaction?

S14.2.1

Reactant concentrations are highest at the beginning of a reaction. The plot of [C] versus t is a curve with a slope that becomes steadily less positive.

Q14.2.2

Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?

Q14.2.3

Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of 10^{10} L/(mol·s). Are the reactions expected to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $H_3O^+ + OH^- \rightarrow 2H_2O$ and $H_3O^+ + N(CH_3)_3 \rightarrow H_2O + HN(CH_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?

S14.2.3

Faster in a less viscous solvent because the rate of diffusion is higher; the H_3O^+/OH^- reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.

Q14.2.4

What information can be obtained from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?

Q14.2.5

During the hydrolysis reaction A + H_2O → B + C, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How would this effect be reflected in the overall reaction order?

Q14.2.6

The reaction rate of a particular reaction in which A and B react to make C is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{2}\left(\frac{\Delta[\text{C}]}{\Delta t}\right)$$

Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

Q14.2.7

While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?

Q14.2.8

Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

Time (s)	[A] (M)
120	0.158
240	0.089
360	0.062

Q14.2.9

Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.

a. C_2H_5I → C_2H_4 + HI: rate = $k[C_2H_5I]$
b. SO + O_2 → SO_2 + O: rate = k[SO][O_2]
c. $2CH_3$ → C_2H_6: rate = $k[CH_3]^2$
d. ClOO → Cl + O_2: rate = k

Q14.2.10

Cleavage of C_2H_6 to produce two CH_3· radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with k = 5.46×10^{-4} s^{-1}. How long will it take for the reaction to go to 15% completion? to 50% completion?

S14.2.10

298 s; 1270 s

Q14.2.11

Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.

$$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+ \tag{1.E.1}$$

$$O_2^+ + O \xrightarrow{k_2} O_2 + O^+ \tag{1.E.2}$$

$$(O^+ + N_2 \xrightarrow{k_3} NO^+ + N \tag{1.E.3}$$

Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[N_2^+][O_2]$, which one of the steps is rate limiting?

Q14.2.12

The oxidation of aqueous iodide by arsenic acid to give I_3^- and arsenous acid proceeds via the following reaction:

$$H_3AsO_4(aq) + 3I^-(aq) + 2H^+(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_3AsO_3(aq) + I_3^-(aq) + H_2O(l)$$

Write an expression for the initial rate of decrease of $[I_3^-]$, $\Delta[I_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [H_3AsO_3][I_3^-]/[H_3AsO_4][I^-]^3[H^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

14.3: Concentration and Rate

14.4: The Change of Concentration with Time

Q14.4.1

What are the characteristics of a zeroth-order reaction? Experimentally, how would you determine whether a reaction is zeroth order?

Q14.4.2

Predict whether the following reactions are zeroth order and explain your reasoning.

a. a substitution reaction of an alcohol with HCl to form an alkyl halide and water
b. catalytic hydrogenation of an alkene
c. hydrolysis of an alkyl halide to an alcohol
d. enzymatic conversion of nitrate to nitrite in a soil bacterium

Q14.4.3

In a first-order reaction, what is the advantage of using the integrated rate law expressed in natural logarithms over the rate law expressed in exponential form?

Q14.4.4

If the reaction rate is directly proportional to the concentration of a reactant, what does this tell you about (a) the reaction order with respect to the reactant and (b) the overall reaction order?

Q14.4.5

The reaction of NO with O_2 is found to be second order with respect to NO and first order with respect to O_2. What is the overall reaction order? What is the effect of doubling the concentration of each reagent on the reaction rate?

Q14.4.6

Iodide reduces Fe(III) according to the following reaction:

$$2Fe^{3+}(soln) + 2I^-(soln) \rightarrow 2Fe^{2+}(soln) + I_2(soln) \tag{1.E.4}$$

Experimentally, it was found that doubling the concentration of Fe(III) doubled the reaction rate, and doubling the iodide concentration increased the reaction rate by a factor of 4. What is the reaction order with respect to each species? What is the overall rate law? What is the overall reaction order?

S14.4.6

First order in Fe^{3+}; second order in I^-; third order overall; rate = $k[Fe^{3+}][I^-]^2$.

Q14.4.7

Benzoyl peroxide is a medication used to treat acne. Its rate of thermal decomposition at several concentrations was determined experimentally, and the data were tabulated as follows:

Experiment	[Benzoyl Peroxide]$_0$ (M)	Initial Rate (M/s)
1	1.00	2.22×10^{-4}
2	0.70	1.64×10^{-4}
3	0.50	1.12×10^{-4}
4	0.25	0.59×10^{-4}

What is the reaction order with respect to benzoyl peroxide? What is the rate law for this reaction?

S14.4.7

The general rate law is: rate = k [Benzoyl Peroxide]^m. In order to find the reaction order with respect to benzoyl peroxide, divide two rate laws and solve for m:

$$\frac{rate_2}{rate_1} = \frac{k_2}{k_1}\left(\frac{[BenzoylPeroxide]_2}{[BenzoylPeroxide]_1}\right)^m$$

$$\frac{1.64 \times 10^{-4}\frac{M}{s}}{2.22 \times 10^{-4}\frac{M}{s}} = (\frac{0.070M}{1.00M})^m$$

$$0.738 = (0.7)^m$$

$$m = 0.85$$

rate law: rate = k [Benzoyl Peroxide]$^{0.85}$

Q14.4.8

1-Bromopropane is a colorless liquid that reacts with $S_2O_3^{2-}$ according to the following reaction:

$$C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^- + Br^- \tag{1.E.5}$$

The reaction is first order in 1-bromopropane and first order in $S_2O_3^{2-}$, with a rate constant of 8.05×10^{-4} $M^{-1}{\cdot}s^{-1}$. If you began a reaction with 40 mmol/100 mL of C_3H_7Br and an equivalent concentration of $S_2O_3^{2-}$, what would the initial reaction rate be? If you were to decrease the concentration of each reactant to 20 mmol/100 mL, what would the initial reaction rate be?

S14.4.8

1.29×10^{-4} M/s; 3.22×10^{-5} M/s

Q14.4.9

The experimental rate law for the reaction 3A + 2B → C + D was found to be $\Delta[C]/\Delta t = k[A]^2[B]$ for an overall reaction that is third order. Because graphical analysis is difficult beyond second-order reactions, explain the procedure for determining the rate law experimentally.

14.5: Temperature and Rate

Q14.5.1

Although an increase in temperature results in an increase in kinetic energy, this increase in kinetic energy is not sufficient to explain the relationship between temperature and reaction rates. How does the activation energy relate to the chemical kinetics of a reaction? Why does an increase in temperature increase the reaction rate despite the fact that the average kinetic energy is still less than the activation energy?

S14.5.1

Activation energy is required for a collision between molecules to result in a chemical reaction, as well it is related to the rate due to the Arrhenius equation

Activation energy is the threshold of energy needed in order for a reaction to occur. Reactant particles must collide with enough energy to be able to break chemical bonds, that will then allow the creation of new bonds. If the particles do not have enough energy, when they collide they will simply bounce off one another.

$k=Ae^{(-Ea/RT)}$. The increase in temperature increases the rate of reaction despite the fact the average kinetic is less than the activation energy since it increase the rate of collision between molecules.

With an increase in temperature, there is a greater distribution of kinetic energy among reactant particles. This increase of temperature allows the rate in which particles collide with one another to increase. Although the average kinetic energy is still lower than the activation energy, the increase of collisions among particles increases the chance of particles that contain enough energy to overcome the energy barrier to collide. Thus, the reaction rate increases due to this increased rate of collisions.

Additionally, there is a higher amount of molecules that have sufficient kinetic energy to overcome the energy barrier, despite the average energy of all these molecules still being lower than the activation energy.

Q14.5.2

For any given reaction, what is the relationship between the activation energy and each of the following?

a. electrostatic repulsions
b. bond formation in the activated complex
c. the nature of the activated complex

S14.5.2

1.) Electrostatic repulsion: Electrostatic repulsion is the unfavorable interaction between two species of like charge. Activation energy is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed.

2.) Bond formation in the activated complex: An activated complex is an intermediate state that is formed during the conversion of reactants into products. Bond breaking can increase activation energy as breaking bonds requires energy.

3.) Nature of the activated complex: The activation energy of a chemical reaction is the difference between the energy of the activated complex and the energy of the reactants. If the structure has a high steric hindrance the activation energy will be higher.

Q14.5.3

If you are concerned with whether a reaction will occur rapidly, why would you be more interested in knowing the magnitude of the activation energy than the change in potential energy for the reaction?

Q14.5.4

The product C in the reaction A + B → C + D can be separated easily from the reaction mixture. You have been given pure A and pure B and are told to determine the activation energy for this reaction to determine whether the reaction is suitable for the industrial synthesis of C. How would you do this? Why do you need to know the magnitude of the activation energy to make a decision about feasibility?

Q14.5.5

Above E_a, molecules collide with enough energy to overcome the energy barrier for a reaction. Is it possible for a reaction to occur at a temperature less than that needed to reach E_a? Explain your answer.

Q14.5.6

What is the relationship between A, E_a, and T? How does an increase in A affect the reaction rate?

Q14.5.7

Of two highly exothermic reactions with different values of E_a, which would need to be monitored more carefully: the one with the smaller value or the one with the higher value? Why?

Q14.5.8

What happens to the approximate rate of a reaction when the temperature of the reaction is increased from 20°C to 30°C? What happens to the reaction rate when the temperature is raised to 70°C? For a given reaction at room temperature (20°C), what is the shape of a plot of reaction rate versus temperature as the temperature is increased to 70°C?

S14.5.8

The reaction rate will approximately double: 20°C to 30°C, the reaction rate increases by about $2^1 = 2$; 20°C to 70°C, the reaction rate increases by about $2^5 = 32$-fold. A plot of reaction rate versus temperature will give an exponential increase: rate $\propto 2^{\Delta T/10}$.

Q14.5.9

Acetaldehyde, used in silvering mirrors and some perfumes, undergoes a second-order decomposition between 700 and 840 K. From the data in the following table, would you say that acetaldehyde follows the general rule that each 10 K increase in temperature doubles the reaction rate?

T (K)	k ($M^{-1}·s^{-1}$)
720	0.024
740	0.051
760	0.105
800	0.519

Q14.5.10

Bromoethane reacts with hydroxide ion in water to produce ethanol. The activation energy for this reaction is 90 kJ/mol. If the reaction rate is 3.6×10^{-5} M/s at 25°C, what would the reaction rate be at the following temperatures?

a. 15°C
b. 30°C
c. 45°C

Q14.5.11

An enzyme-catalyzed reaction has an activation energy of 15 kcal/mol. How would the value of the rate constant differ between 20°C and 30°C? If the enzyme reduced the E_a from 25 kcal/mol to 15 kcal/mol, by what factor has the enzyme increased the reaction rate at each temperature?

S14.5.11

a. 1.0×10^{-5} M/s
b. 6.6×10^{-5} M/s
c. 3.5×10^{-4} M/s

Q14.5.12

The data in the following table are the rate constants as a function of temperature for the dimerization of 1,3-butadiene. What is the activation energy for this reaction?

T (K)	k ($M^{-1}·min^{-1}$)
529	1.4
560	3.7
600	25
645	82

S14.5.12

100 kJ/mol

Q14.5.13

The reaction rate at 25°C is 1.0×10^{-4} M/s. Increasing the temperature to 75°C causes the reaction rate to increase to 7.0×10^{-2} M/s. Estimate E_a for this process. If E_a were 25 kJ/mol and the reaction rate at 25°C is 1.0×10^{-4} M/s, what would be the reaction rate at 75°C?

14.6: Reaction Mechanisms

Q14.6.1

How does the term molecularity relate to elementary reactions? How does it relate to the overall balanced chemical equation?

Q14.6.2

What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?

Q14.6.3

When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?

Q14.6.3

If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?

Q14.6.4

Give the rate-determining step for each case.

a. Traffic is backed up on a highway because two lanes merge into one.
b. Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
c. A document containing text and graphics is downloaded from the Internet.

Q14.6.5

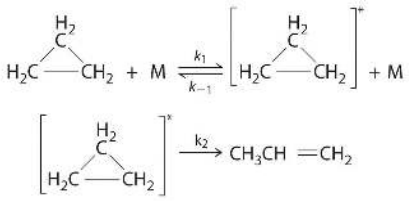
Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

S14.6.5

Free radicals are uncharged molecules with an unpaired valence electron. The reason these are so dangerous is because they like to grab electrons from other atoms to fill their own outer shell. This allows them to impair protein function because free radicals readily oxidize proteins and cell membrane which could lead to a loss of function. It was important to purge James Bond of radicals because radicals set off chain reactions of continuously pulling electrons from molecules, which in turn, can damage cells in the body.

Q14.6.6

Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



where M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

S14.6.6

When we are trying to decide which step is a rate-determining step, you have to look at which step is the slowest of them all, since we have no knowledge of the time scale for either of these steps we have to look elsewhere to determine the rate-determining step.

In our specific problem, we do not know what exact molecules we have however we do see that the first step is an equilibrium since it has a double-headed arrow with two k values one that is the reciprocal of the other. Since it is an equilibrium we can reasonably assume that energized propane is rapidly created which would lead us to the conclusion that the second step is the slower of the two steps and is, therefore, the rate-determining step. So, the second step (with k_2) determines the rate constant of the overall reaction.

Q14.6.7

Above approximately 500 K, the reaction between NO_2 and CO to produce CO_2 and NO follows the second-order rate law $\Delta[CO_2]/\Delta t = k[NO_2][CO]$. At lower temperatures, however, the rate law is $\Delta[CO_2]/\Delta t = k'[NO_2]^2$, for which it is known that NO_3 is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?

S14.6.7

Given that NO_3 is an intermediate in the low temperature reaction mechanism, we automatically know two things: 1) *NO_3 won't show up in the final overall reaction*, and thus, 2) *NO_3 will be in the products of the first reaction of the mechanism and in the reactants of the second reaction*. We can also assume that since we're given an intermediate from the problem, this is the only intermediate (so we won't have to dream up any other compounds that might exist in the series of reactions.) These things being said, the **lower temperature reaction mechanism** will look like this:

$$2NO_2(g) \rightarrow NO_3(g) + NO(g) \quad (1)$$

$$CO(g) + NO_3(g) \rightarrow CO_2(g) + NO_2(g) \quad (2)$$

And the overall reaction will look like this (notice how NO_3 is not present):

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g) \quad \textbf{(overall reaction)}$$

Now that we have the reaction mechanism written out, we can go about determining which step is the slowest. It would be pretty tricky to do this if we weren't given any further information, however, we know two more things: 1) *the high-temperature mechanism's rate = $k[NO_2][CO]$ meaning that it took place in one step* (given that the overall reaction is also equal to this rate) and 2) *the low-temperature mechanism's rate = $k'[NO_2]^2$*. These two things being said, we've both confirmed that our proposed low-temperature reaction mechanism is in fact two steps, and that *we have a means to find which step is slower*.

By using the "guess-and-check" method we can label each step reaction one at a time as the **"slow reaction"** and see if the rate matches up with the rate given to us.

Let's first try the 2nd reaction. (see above)

By using rate laws we can determine that the rate of the reaction must be in terms of its reactants, which follows:

$$k[CO][NO_3] \tag{1.E.6}$$

... *But wait!* We can't have the overall reaction rate in terms of an intermediate.

By looking at the 1st reaction, we can determine that we can sub in "$[NO_2]$ /[NO]" for "$[NO_3]$" since by writing the full reaction rate of the first step and solving for $[NO_3]$ this is equivalent. So, we now have the overall rate of the mechanism as the following given the 2nd reaction is the "slow reaction:"

$$k\frac{[CO][NO_2]^2}{[NO]} \tag{1.E.7}$$

Note that NO_2 is raised to the second power to account for the stoichiometry of the balanced reaction.

So clearly the 2nd reaction isn't the slow reaction since the rate is not equivalent to what we were given!

Let's check the rate of the 1st reaction now...

$$k[NO_2]^2 \tag{1.E.8}$$

What do you know... the rates are equal!

We have now confirmed that the 1st reaction is the slow reaction equation, since its rate is equivalent to the overall reaction rate.

Q14.6.8

Nitramide (O_2NNH_2) decomposes in aqueous solution to N_2O and H_2O. What is the experimental rate law ($\Delta[N_2O]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?

$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+$	(fast)
$O_2NNH^- \xrightarrow{k_2} N_2O + OH^-$	(slow)
$H^+ + OH^- \xrightarrow{k_3} H_2O$	(fast)

Assume that the rates of the forward and reverse reactions in the first equation are equal.

S14.6.8

We know that the slowest step of the reaction is the rate determining step, since it usually has the highest activation energy requirement. As a result, the slowest step of the reaction is the experimental rate law we are looking for.

Note: since the slowest step is the rate determining step, that usually means there is some intermediate in between. Intermediates should NEVER be a part of the rate law mechanism.

$$rate = rate_2 = k_2[O_2NNH^-] \tag{1.E.9}$$

Since Nitramide is an intermediate, we must find some way to substitute it. To solve that problem, we look for where Nitramide is produced and consumed. We see that

$$rate_1 = k_1[O_2NNH_2] \tag{1.E.10}$$

$$rate_{-1} = k_{-1}[O_2NNH^-][H^+] \tag{1.E.11}$$

Since these two rates produce and consume the same amount of O_2NNH^- over the same time period, we can set them equal to each other and solve for the intermediate

$$rate_1 = rate_{-1} \tag{1.E.12}$$

$$k_1[O_2NNH_2] = k_{-1}[O_2NNH^-][H^+] \tag{1.E.13}$$

$$[O_2NNH^-] = \frac{k_1[O_2NNH_2]}{k_{-1}[H^+]} \tag{1.E.14}$$

Substituting this equation back into our original equation gives us

$$rate = rate_2 = k_2\frac{k_1[O_2NNH_2]}{k_{-1}[H^+]} \tag{1.E.15}$$

With all of the rate constants (k), we can clean up our equation a little bit by saying

$$k = \frac{k_2k_1}{k_{-1}} \tag{1.E.16}$$

Leaving us with

$$rate = \frac{k[O_2NNH_2]}{[H^+]} \tag{1.E.17}$$

A14.6.8

$$\text{rate} = k_2\frac{k_1[\text{O}_2\text{NNH}_2]}{k_{-1}[\text{H}^+]} = k\frac{[\text{O}_2\text{NNH}_2]}{[\text{H}^+]}$$

Q14.6.9

The following reactions are given:

$$\text{A} + \text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{C} + \text{D} \tag{1.E.18}$$

$$\text{D} + \text{E} \xrightarrow{k_2} \text{F} \tag{1.E.19}$$

What is the relationship between the relative magnitudes of k_{-1} and k_2 if these reactions have the following rate law?

$$\frac{\Delta[F]}{\Delta t} = k\frac{[A][B][E]}{[C]} \tag{1.E.20}$$

How does the magnitude of k_1 compare to that of k_2? Under what conditions would you expect the rate law to be

$$\frac{\Delta[F]}{\Delta t} = k'[A][B]? \tag{1.E.21}$$

Assume that the rates of the forward and reverse reactions in the first equation are equal.

S14.6.9

First, because we have broken the equations down into elementary steps we can write the rate laws for each step.

Step1:

$$A + B \xrightarrow{k_1} C + D \tag{1.E.22}$$

$$rate = k_1[A][B] \tag{1.E.23}$$

Step 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{1.E.24}$$

$$rate = k_{-1}[C][D] \tag{1.E.25}$$

Step 3:

$$D + E \xrightarrow{k_2} F \tag{1.E.26}$$

$$rate = k_2[D][E] \tag{1.E.27}$$

If we add a these steps together we see that we get overall reaction

$$A + B + E \rightarrow C + F \tag{1.E.28}$$

we can see that [D] is an intermediate and

$$k_1 = k_{-1} \tag{1.E.29}$$

.

Since we are not told which steps are fast or slow we need to use Steady State Approximation.

If the second step is the slower step ($k_{-1} >> k_2$) then our rate determining step would be

$$rate = k_2[D][E] \tag{1.E.30}$$

Since we can only write rate laws in terms of products and reactants we have to rewrite this so that we are not including an intermediate.

Assume: rate of [D] formation = rate of its disappearance

$$k_1[A][B] = k_{-1}[C][D] + k_2[D][E] \tag{1.E.31}$$

$$k_1[A][B] = [D](k_{-1}[C] + k_2[E]) \tag{1.E.32}$$

Solving for [D] we find that

$$[D] = \frac{k_1[A][B]}{(k_{-1}[C] + k_2[E])} \tag{1.E.33}$$

now we can use this to substitute the intermediate [D] in the rate law to get an appropriate rate law.

$$rate = \frac{k_2 k_1[A][B][E]}{(k_{-1}[C] + k_2[E])} \tag{1.E.34}$$

because we had already established $k_{-1} >> k_2$ *we can assume that*

$$k_{-1}[C] + k_2[E] \approx k_{-1}[C] \tag{1.E.35}$$

this would give us the observed rate law

$$\frac{\Delta[F]}{\Delta t} = \frac{k_2 k_1[A][B][E]}{k_{-1}[C]} \tag{1.E.36}$$

to make this clearer we can set

$$k = \frac{(k_2)(k_1)}{(k_{-1})} \tag{1.E.37}$$

and we can then simplify it down to

$$\frac{\Delta[F]}{\Delta t} = k\frac{[A][B][E]}{[C]} \tag{1.E.38}$$

we can see that all of these rate constants are related by this ratio k_2k_1/k_{-1}. Since k_2 is our rate determining step $k_{-1} >> k_2$ *and since* $k_1 = k_{-1}$ then we can see that $k_1 >> k_2$.

We would expect the rate law to be

$$\frac{\Delta[F]}{\Delta t} = k'[A][B]? \tag{1.E.39}$$

if the rate determining step aka the slowest step is that corresponding to (step 1) since the rate law for this step is k_1[A][B] and this is the exact the same as the rate law that we were given.

14.7: Catalysis

Q14.7.1

What effect does a catalyst have on the activation energy of a reaction? What effect does it have on the frequency factor (*A*)? What effect does it have on the change in potential energy for the reaction?

S14.7.1

A catalyst lowers the activation energy of a reaction. Some catalysts can also orient the reactants and thereby increase the frequency factor. Catalysts have no effect on the change in potential energy for a reaction.

Q14.7.2

How is it possible to affect the product distribution of a reaction by using a catalyst?

Q14.7.3

A heterogeneous catalyst works by interacting with a reactant in a process called *adsorption*. What occurs during this process? Explain how this can lower the activation energy.

S14.7.3

In adsorption, a reactant binds tightly to a surface. Because intermolecular interactions between the surface and the reactant weaken or break bonds in the reactant, its reactivity is increased, and the activation energy for a reaction is often decreased.

Q14.7.4

What effect does increasing the surface area of a heterogeneous catalyst have on a reaction? Does increasing the surface area affect the activation energy? Explain your answer.

Q14.7.5

Identify the differences between a heterogeneous catalyst and a homogeneous catalyst in terms of the following.

a. ease of recovery
b. collision frequency
c. temperature sensitivity
d. cost

S14.7.4

a. Heterogeneous catalysts are easier to recover.
b. Collision frequency is greater for homogeneous catalysts.
c. Homogeneous catalysts are often more sensitive to temperature.
d. Homogeneous catalysts are often more expensive.

Q14.7.6

An area of intensive chemical research involves the development of homogeneous catalysts, even though homogeneous catalysts generally have a number of operational difficulties. Propose one or two reasons why a homogenous catalyst may be preferred.

S14.7.6

Catalysts are compounds that, when added to chemical reactions, reduce the activation energy and increase the reaction rate. The amount of a catalyst does not change during a reaction, as it is not consumed as part of the reaction process. Catalysts lower the energy required to reach the transition state of the reaction, allowing more molecular interactions to achieve that state. However, catalysts do not affect the degree to which a reaction progresses. In other words, though catalysts affect reaction kinetics, the equilibrium state remains unaffected.

Catalysts can be classified into two types: homogenous and heterogeneous. Homogenous catalysts are those which exist in the same phase (gas or liquid) as the reactants, while heterogeneous catalysts are not in the same phase as the reactants. Typically, heterogeneous catalysis involves the use of solid catalysts placed in a liquid reaction mixture. For this question, we will be discussing homogenous catalysts.

Most of the times, homogeneous catalysis involves the introduction of an aqueous phase catalyst into an aqueous solution of reactants. One reason why homogeneous catalysts are preferred over heterogeneous catalysts because homogeneous catalysts mix well in chemical reactions in comparison to heterogeneous catalysts. However, homogeneous catalyst is often irrecoverable after the reaction has run to completion.

Q14.7.7

Consider the following reaction between cerium(IV) and thallium(I) ions:

$$2\,Ce^{4+} + Tl^{+} \longrightarrow 2\,Ce^{3+} + Tl^{3+} \tag{1.E.40}$$

This reaction is slow, but Mn^{2+} catalyzes it, as shown in the following mechanism:

$$Ce^{4+} + Mn^{2+} \longrightarrow Ce^{3+} + Mn^{3+} \tag{1.E.41}$$

$$Ce^{4+} + Mn^{3+} \longrightarrow Ce^{3+} + Mn^{4+} \tag{1.E.42}$$

$$Mn^{4+} + Tl^{+} \longrightarrow Tl^{3+} + Mn^{2+} \tag{1.E.43}$$

In what way does Mn^{2+} increase the reaction rate?

S14.7.7

The Mn^{2+} ion donates two electrons to Ce^{4+}, one at a time, and then accepts two electrons from Tl^{+}. Because Mn can exist in three oxidation states separated by one electron, it is able to couple one-electron and two-electron transfer reactions.

Q14.7.8

The text identifies several factors that limit the industrial applications of enzymes. Still, there is keen interest in understanding how enzymes work for designing catalysts for industrial applications. Why?

S14.7.8

Enzymes are expensive to make, denature and fail at certain temperatures, are not that stable in a solution, and are very specific to the reaction it was made for. However, scientists can use the observations from enzymes to create catalysts that are more effective in aiding the reaction and cost less to produce. Overall, catalysts still play a large part in lowering the activation energy for reactions. Creating new catalysts can help in the improvement of areas such as medical, ecological, and even commercial products.

Q14.7.9

Most enzymes have an optimal pH range; however, care must be taken when determining pH effects on enzyme activity. A decrease in activity could be due to the effects of changes in pH on groups at the catalytic center or to the effects on groups located elsewhere in the enzyme. Both examples are observed in chymotrypsin, a digestive enzyme that is a protease that hydrolyzes polypeptide chains. Explain how a change in pH could affect the catalytic activity due to (a) effects at the catalytic center and (b) effects elsewhere in the enzyme. (*Hint*: remember that enzymes are composed of functional amino acids.)

Q14.7.10

At some point during an enzymatic reaction, the concentration of the activated complex, called an enzyme–substrate complex (***ES***), and other intermediates involved in the reaction is nearly constant. When a single substrate is involved, the reaction can be represented by the following sequence of equations:

$$\begin{aligned}\text{enzyme (E)} + \text{substrate (S)} &\rightleftharpoons \text{enzyme-substrate complex (ES)} \\ &\rightleftharpoons \text{enzyme (E)} + \text{product (P)}\end{aligned} \tag{1.E.44}$$

This can also be shown as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P \tag{1.E.45}$$

Using molar concentrations and rate constants, write an expression for the rate of disappearance of the enzyme–substrate complex. Typically, enzyme concentrations are small, and substrate concentrations are high. If you were determining the rate law by varying the substrate concentrations under these conditions, what would be your apparent reaction order?

S14.7.10

$\frac{\Delta[ES]}{\Delta t} = -(k_2 + k_{-1})[ES] + k_1[E][S] + k_{-2}[E][P] \approx 0$; zeroth order in substrate.

Q14.7.11

A particular reaction was found to proceed via the following mechanism:

- $A + B \rightarrow C + D$ (slow)
- $2C \rightarrow E$ (fast)
- $E + A \rightarrow B + F$ (fast)

What is the overall reaction? Is this reaction catalytic, and if so, what species is the catalyst? Identify the intermediates

Q14.7.12

A particular reaction has two accessible pathways (A and B), each of which favors conversion of *X* to a different product (*Y* and *Z*, respectively). Under uncatalyzed conditions pathway A is favored, but in the presence of a catalyst pathway B is favored. Pathway B is reversible, whereas pathway A is not. Which product is favored in the presence of a catalyst? without a catalyst? Draw a diagram illustrating what is occurring with and without the catalyst.

S14.7.12

In both cases, the product of pathway A is favored. All of the *Z* produced in the catalyzed reversible pathway B will eventually be converted to *X* as *X* is converted irreversibly to *Y* by pathway A.

Q14.7.13

The kinetics of an enzyme-catalyzed reaction can be analyzed by plotting the reaction rate versus the substrate concentration. This type of analysis is referred to as a Michaelis–Menten treatment. At low substrate concentrations, the plot shows behavior characteristic of first-order kinetics, but at very high substrate concentrations, the behavior shows zeroth-order kinetics. Explain this phenomenon.

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CHAPTER OVERVIEW

2: Chemical Equillibrium

2.1: The Concept of Equilibrium
2.2: The Equilibrium Constant (K)
2.3: Expressing the Equilibrium Constant in Terms of Pressure
2.4: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations
2.5: Heterogeneous Equilibria (when reactants are in more than one phase)
2.6: Finding Equilibrium Concentrations
2.7: The Reaction Quotient- Predicting the Direction of Change
2.8: Le Châtelier's Principle- How a System at Equilibrium Responds to Disturbances
2.E: Chemical Equilibrium (Practice Problems with Answers)

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2.1: The Concept of Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.



Figure **2.1.1**: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($\mathbf{N_2O_4}$) to nitrogen dioxide ($\mathbf{NO_2}$). You may recall that $\mathbf{NO_2}$ is responsible for the brown color we associate with smog. When a sealed tube containing solid $\mathbf{N_2O_4}$ (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of $\mathbf{NO_2}$ appears (Figure **2.1.1**). The reaction can be followed visually because the product ($\mathbf{NO_2}$) is colored, whereas the reactant ($\mathbf{N_2O_4}$) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{2.1.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \xrightarrow{k_f} 2\,NO_2(g) \tag{2.1.2}$$

and reverse reaction

$$2\,NO_2(g) \xrightarrow{k_r} N_2O_4(g) \tag{2.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure **2.1.2** shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of $\mathbf{NO_2}$ were zero, then it increases as the concentration of $\mathbf{N_2O_4}$ decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no $\mathbf{N_2O_4}$ but an

initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure **2.1.2***a*), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure **2.1.2***b*). Thus equilibrium can be approached from either direction in a chemical reaction.

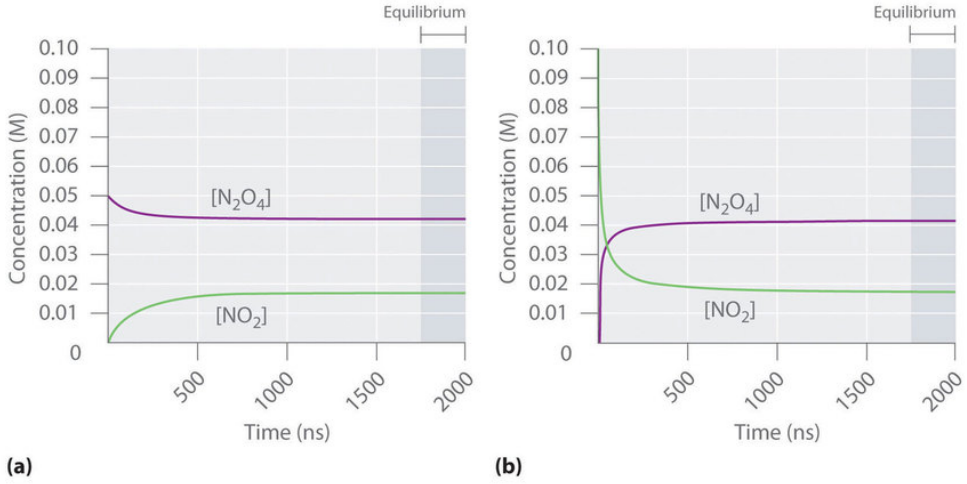


Figure **2.1.2**: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure **2.1.3** shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6\ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 2.1.1 and 2.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

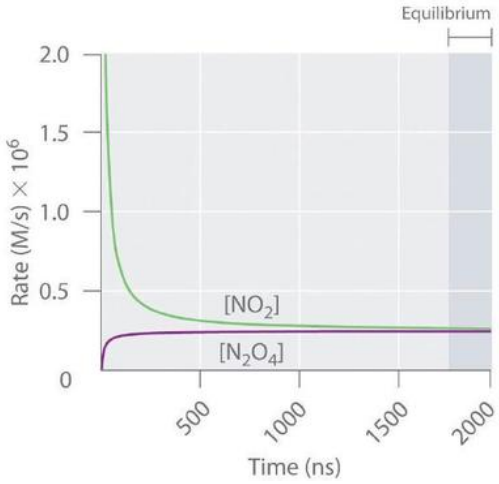


Figure **2.1.3**: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure **2.1.2**. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

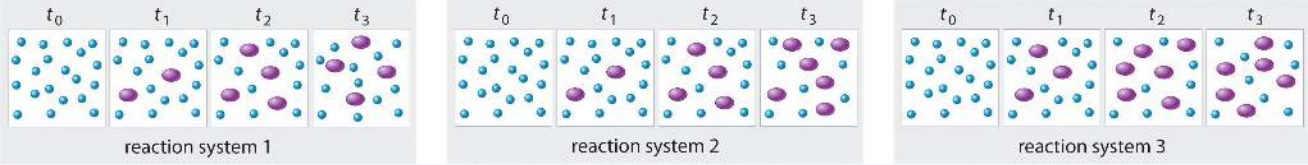
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 2.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

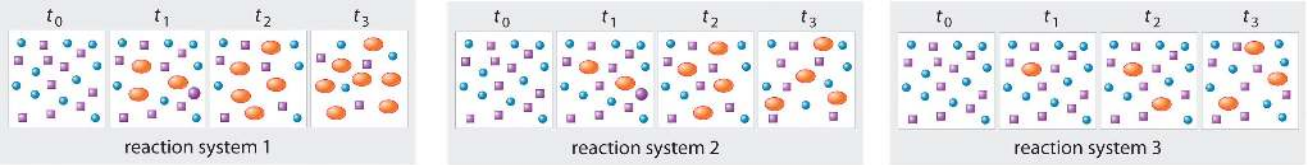
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 2.1.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer

system 2



A Video Introduction to Dynamic Equilibrium: https://youtu.be/4AJbFuzW2cs

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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2.2: The Equilibrium Constant (K)

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of $\mathbf{N_2O_4}$ to $\mathbf{NO_2}$. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[\mathrm{N_2O_4}]$$

and

$$\text{reverse rate} = k_r[\mathrm{NO_2}]^2$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[\mathrm{N_2O_4}] = k_r[\mathrm{NO_2}]^2 \tag{2.2.1}$$

so

$$\frac{k_f}{k_r} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{2.2.2}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{2.2.3}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> *The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.*



A Video for Determining the Equilibrium Expression: Determining the Equilibrium Expression(opens in new window) [youtu.be]

Table **2.2.1** lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 2.2.1. At equilibrium the magnitude of the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of $\mathbf{NO_2}$ and $\mathbf{N_2O_4}$ are, at equilibrium the quantity $[\mathrm{NO_2}]^2/[\mathrm{N_2O_4}]$ will always be $\mathbf{6.53 \pm 0.03}$

$\times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 2.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

[\(\ce{NO2}\)] (M)	Initial Concentrations [\(\ce{NO2}\)] (M)		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{2.2.4}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action (or law of chemical equilibrium) and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2.2.5}$$

where K is the equilibrium constant for the reaction. Equation 2.2.4 is called the equilibrium equation, and the right side of Equation 2.2.5 is called the equilibrium constant expression. The relationship shown in Equation 2.2.5 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 2.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 2.2.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Effective vs. True Concentrations

You will also notice in Table **2.2.2** that equilibrium constants have no units, even though Equation 2.2.5 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 2.2.6, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{2.2.6}$$

Because equilibrium constants are calculated using "effective concentrations" relative to a standard state of 1 M, values of K are unitless.

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form **HD**:

$$\mathrm{H_2\,(g) + D_2\,(g) \rightleftharpoons 2\,HD\,(g)}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure **2.2.3** summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 2.2.6 and 2.2.5), when $k_f \gg k_r$, K is a **large**

number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

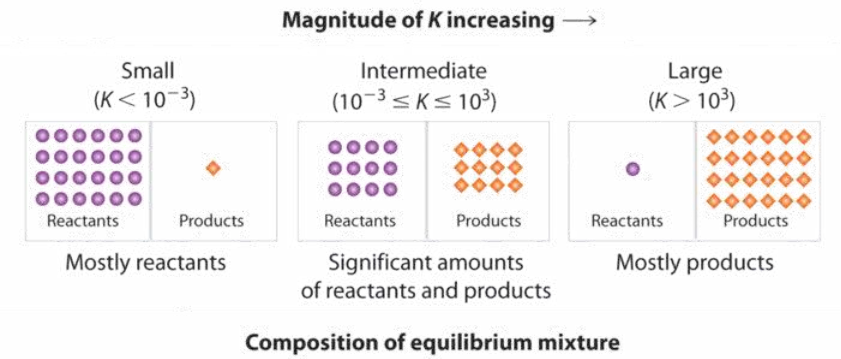


Figure **2.2.3**: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

If K is less than 0.001, it is considered small and it will be mostly reactants. If K is greater than 1000, it is considered large and it will be mostly products. If K is greater than or equal to 0.001 and less than or equal to 1000, it is considered intermediate. there will be significant amounts or reactants and products.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

✔ Example 2.2.1: Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

- $\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)}$
- $\mathrm{CO(g) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons CO_2(g)}$
- $\mathrm{2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 2.2.5. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, $\mathrm{N_2}$ has a coefficient of 1 and $\mathrm{H_2}$ has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and $\mathrm{O_2}$, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[\mathrm{CO_2}]}{[\mathrm{CO}][\mathrm{O_2}]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for $\mathrm{O_2}$. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

Exercise 2.2.1

Write the equilibrium constant expression for each reaction.

a. $\mathrm{N_2O\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + \frac{1}{2}\,\mathrm{O_2\,(g)}$
b. $\mathrm{2\,C_8H_{18}\,(g)} + \mathrm{25\,O_2\,(g)} \rightleftharpoons \mathrm{16\,CO_2\,(g)} + \mathrm{18\,H_2O\,(g)}$
c. $\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons \mathrm{2\,HI\,(g)}$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Example 2.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 2.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

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

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,

- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C



Video which Discusses What Does K Tell us About a Reaction?: What Does K Tell us About a Reaction?(opens in new window) [youtu.be]

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 2.2.4 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{2.2.7}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{2.2.8}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $\mathrm{N_2O_4} \rightleftharpoons 2\,\mathrm{NO_2}$ is as follows:

$$K = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{2.2.9}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{2.2.10}$$

Consider another example, the formation of water:

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \rightleftharpoons 2\,\mathrm{H_2O\,(g)}.$$

Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> *The equilibrium constant for a reaction written in reverse is the inverse of the equilibrium constant for the reaction as written originally.*

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2\,NO_2 \rightleftharpoons N_2O_4$$

as

$$NO_2 \rightleftharpoons \tfrac{1}{2}\,N_2O_4$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{2.2.11}$$

The values for K′ (Equation 2.2.10) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{2.2.12}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the n^{th} power.



A Video Discussing Relationships Involving Equilibrium Constants: Relationships Involving Equilibrium Constants(opens in new window) [youtu.be] (opens in new window)

Example 2.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

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

What is the equilibrium constant for each related reaction at 745 K?

a. $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$
b. $\tfrac{1}{2}\,N_2\,(g) + \tfrac{3}{2}\,H_2\,(g) \rightleftharpoons NH_3\,(g)$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_3\,(g) \rightleftharpoons SO_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

Answer

3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{2.2.13}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{2.2.14}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The “effective pressure” is called the fugacity, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{2.2.15}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of **gaseous** products and **gaseous** reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 2.2.15, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

\[K_p = K(RT)^1 = KRT \nonumber \]

Example 2.2.4: The Haber Process (again)

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

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

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 2.2.15 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 2.2.12, we have the following:

$$\begin{aligned} K_p &= K(RT)^{-2} \\ &= \frac{K}{(RT)^2} \\ &= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} \\ &= 3.16 \times 10^{-5} \end{aligned}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise 2.2.4

Calculate K_p for the reaction

$$\mathrm{2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer

$K_p = 1.2 \times 10^3$



Video Discussing Converting Kc to Kp: Converting Kc to Kp(opens in new window) [youtu.be]

Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of $\mathbf{N_2}$ with $\mathbf{O_2}$ to give $\mathbf{NO_2}$. This reaction is an important source of the $\mathbf{NO_2}$ that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (step 1), $\mathbf{N_2}$ reacts with $\mathbf{O_2}$ at the high temperatures inside an internal combustion engine to give $\mathbf{NO}$. The released $\mathbf{NO}$ then reacts with additional $\mathbf{O_2}$ to give $\mathbf{NO_2}$ (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)} \qquad K_1 = 2.0 \times 10^{-25}$$

$$\mathrm{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)} \quad K_2 = 6.4 \times 10^{9}$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$\mathrm{N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)} \qquad K_3 = ?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.

> *To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.*

Example 2.2.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3}$$

Exercise 2.2.6

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \qquad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \qquad K_3 = ?$

Answer

$K_3 = 1.1 \times 10^{66}$

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas

during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

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2.3: Expressing the Equilibrium Constant in Terms of Pressure

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g)} \tag{2.3.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2} a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{2.3.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{2.3.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 2.3.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 2.3.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

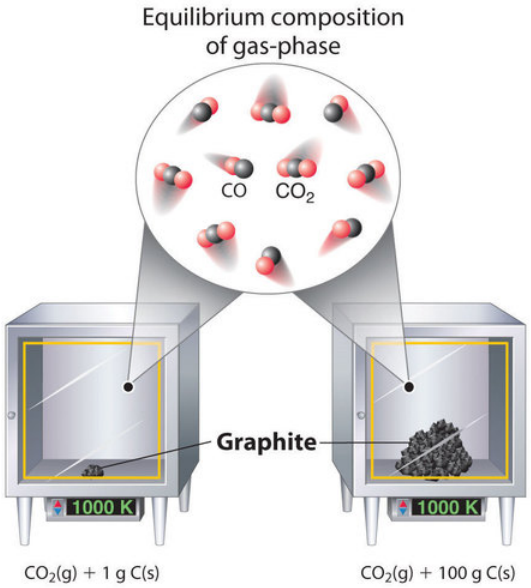


Figure **2.3.2**: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 2.3.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)}$
b. $\mathrm{Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

? Exercise 2.3.1

Write the expressions for K and K_p for the following reactions.

a. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

b. $\underset{glucose}{C_6H_{12}O_6}(s) + 6\,O_2(g) \rightleftharpoons 6\,CO_2(g) + 6\,H_2O(g)$

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

- Anonymous
- Modified by Tom Neils (Grand Rapids Community College)

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2.4: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

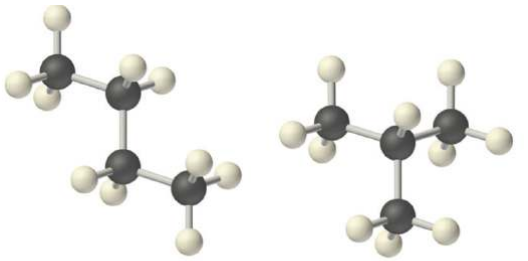
There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



This reaction can be written as follows:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{2.4.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{2.4.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 2.4.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 2.4.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$2NOCl_{(g)} \leftrightharpoons 2NO_{(g)} + Cl_{2(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer

$K = 48.8$ and $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example **2.4.2** shows one way to do this.

✔ Example 2.4.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

\[2 NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}\nonumber \]

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B. Calculate all possible initial concentrations from the data given and insert them in the table.

C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? Exercise 2.4.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$



A Video Disucssing Using ICE Tables to find Kc: Using ICE Tables to find Kc(opens in new window) [youtu.be]

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 2.4.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 2.4.2.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x$$

$$x + 2.6x = 2.6$$

$$x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example **2.4.3** illustrates a common type of equilibrium problem that you are likely to encounter.

Example 2.4.3: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.0150-x)$	$(0.0150-x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(x)(x)}{(0.0150-x)(0.0150-x}=\frac{x^2}{(0.0150-x)^2}=0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2}=\left(\frac{x}{0.0150-x}\right)^2=0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150-x)}=(0.106)^{1/2}=0.326$$

$$x=(0.326)(0.0150)-0.326x$$

$$1.326x=0.00489$$

$$x=0.00369=3.69\times10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f=[H_2]_i+\Delta[H_2]=(0.0150-0.00369)\ M=0.0113\ M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=(0.0150-0.00369)\ M=0.0113\ M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=(0+0.00369)\ M=0.00369\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=(0+0.00369)\ M=0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.00369)^2}{(0.0113)^2}=0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 2.4.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)}+I_{2(g)}\rightleftharpoons 2HI_{(g)}$$

$K=54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f=0.270\ M$
- $[H_2]_f=[I_2]_f=0.037\ M$

In Example **2.4.3**, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the

products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example **2.4.4**.

Example 2.4.4

In the water–gas shift reaction shown in Example **2.4.3**, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example **2.4.3**, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[=[H_2]_i+\Delta[H_2]=0.570\ M-0.148\ M=0.422M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=0.632\ M-0.148\ M=0.484M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=0\ M+0.148\ M=0.148\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=0M+0.148\ M=0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.148)^2}{(0.422)(0.484)}=0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 2.4.4

The exercise in Example 2.4.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K=54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

- $[H_I]_f=0.0882\ M$
- $[H_2]_f=0.156\ M$
- $[I_2]_f=9.2\times10^{-4}M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K\le10^{-3}$) or very large ($K\ge10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 2.4.5.

✔ Example 2.4.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)}+O_{2(g)}\rightleftharpoons2NO_{(g)}$$

with $K_p=2.0\times10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2}=0.78\ atm$ and $P_{O_2}=0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO

produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$
Final	$(0.78-x)$	$(0.21-x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78-x)(0.21-x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78-x) = 0.78$ and $(0.21-x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78-x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21-x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 2.4.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example **2.4.6**.

Example 2.4.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).
C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example **2.4.5**. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	$+x$	$+x$	$-x$
Final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x)$ = 0.045 and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 2.4.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M\ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$



A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: Using ICE Tables to find Eq. Concentrations & Kc(opens in new window) [youtu.be]

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated

from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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2.5: Heterogeneous Equilibria (when reactants are in more than one phase)

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2\,(g) + C\,(s) \rightleftharpoons 2\,CO\,(g)} \tag{2.5.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2} a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{2.5.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{2.5.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 2.5.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 2.5.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

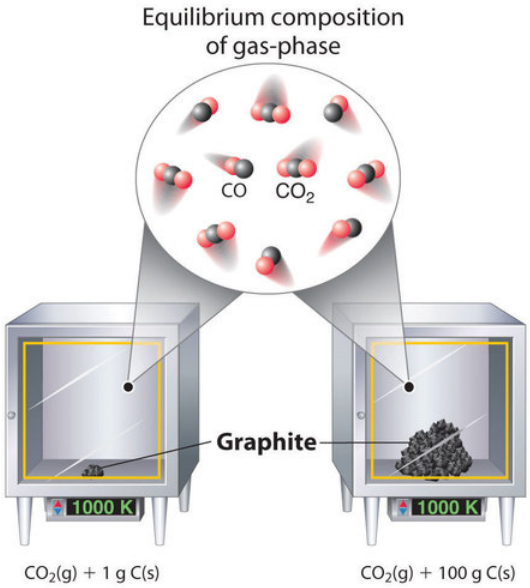


Figure **2.5.2**: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 2.5.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)}$
b. $\mathrm{Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

? Exercise 2.5.1

Write the expressions for K and K_p for the following reactions.

a. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

b. $\underset{glucose}{C_6H_{12}O_6}(s) + 6\,O_2(g) \rightleftharpoons 6\,CO_2(g) + 6\,H_2O(g)$

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

- Anonymous
- Modified by Tom Neils (Grand Rapids Community College)

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2.6: Finding Equilibrium Concentrations

Learning Objectives

- To solve quantitative problems involving chemical equilibriums.

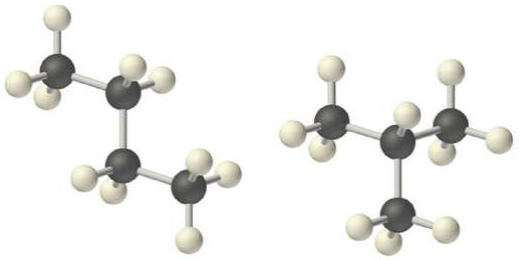
There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).



n-butane isobutane (2-methylpropane)

This reaction can be written as follows:

$$n\text{-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{2.6.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{2.6.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 2.6.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained

- $5.0 \times 10^{-2}\ M\ SO_3$,
- $3.5 \times 10^{-3}\ M\ O_2$, and
- $3.0 \times 10^{-3}\ M\ SO_2$.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4[(0.08206\ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 2.6.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$2NOCl_{(g)} \leftrightharpoons 2NO_{(g)} + Cl_{2(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2}\ M\ HI$,
- $6.47 \times 10^{-3}\ M\ H_2$, and
- $5.94 \times 10^{-4}\ M\ I_2$.

Calculate K and K_p for this reaction.

Answer

$K = 48.8$ and $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 2.6.2 shows one way to do this.

✓ Example 2.6.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

\[2 NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}\nonumber \]

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B. Calculate all possible initial concentrations from the data given and insert them in the table.

C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$. The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$. We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NOCl}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000\ M + 0.056\ M = 0.056\ M$$

$$[NOCl]_f = 0.500\ M + (-0.056\ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? Exercise 2.6.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting $0.1248\ M\ H_2$ and $0.0416\ M\ N_2$ at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer

$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$



A Video Disucssing Using ICE Tables to find Kc: Using ICE Tables to find Kc(opens in new window) [youtu.be]

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 2.6.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 2.6.2.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x$$

$$x + 2.6x = 2.6$$

$$x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example **2.6.3** illustrates a common type of equilibrium problem that you are likely to encounter.

✔ Example 2.6.3: The water–gas shift reaction

The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, K, and initial concentrations

Asked for: final concentrations

Strategy:

A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial	0.0150	0.0150	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.0150-x)$	$(0.0150-x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(x)(x)}{(0.0150-x)(0.0150-x}=\frac{x^2}{(0.0150-x)^2}=0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2}=\left(\frac{x}{0.0150-x}\right)^2=0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150-x)}=(0.106)^{1/2}=0.326$$

$$x=(0.326)(0.0150)-0.326x$$

$$1.326x=0.00489$$

$$x=0.00369=3.69\times10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f=[H_2]_i+\Delta[H_2]=(0.0150-0.00369)\ M=0.0113\ M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=(0.0150-0.00369)\ M=0.0113\ M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=(0+0.00369)\ M=0.00369\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=(0+0.00369)\ M=0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.00369)^2}{(0.0113)^2}=0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 2.6.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)}+I_{2(g)}\rightleftharpoons 2HI_{(g)}$$

$K=54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f=0.270\ M$
- $[H_2]_f=[I_2]_f=0.037\ M$

In Example **2.6.3**, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the

products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example **2.6.4**.

Example 2.6.4

In the water–gas shift reaction shown in Example **2.6.3**, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example **2.6.3**, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f[=[H_2]_i+\Delta[H_2]=0.570\ M-0.148\ M=0.422M$
- $[CO_2]_f=[CO_2]_i+\Delta[CO_2]=0.632\ M-0.148\ M=0.484M$
- $[H_2O]_f=[H_2O]_i+\Delta[H_2O]=0\ M+0.148\ M=0.148\ M$
- $[CO]_f=[CO]_i+\Delta[CO]=0M+0.148\ M=0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K=\frac{[H_2O][CO]}{[H_2][CO_2]}=\frac{(0.148)^2}{(0.422)(0.484)}=0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 2.6.4

The exercise in Example 2.6.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K=54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

- $[H_I]_f=0.0882\ M$
- $[H_2]_f=0.156\ M$
- $[I_2]_f=9.2\times10^{-4}M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K\le10^{-3}$) or very large ($K\ge10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 2.6.5.

✔ Example 2.6.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)}+O_{2(g)}\rightleftharpoons 2NO_{(g)}$$

with $K_p=2.0\times10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2}=0.78\ atm$ and $P_{O_2}=0.21\ atm$?

Given: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO

produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$
Final	$(0.78-x)$	$(0.21-x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78-x)(0.21-x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78-x) = 0.78$ and $(0.21-x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78-x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21-x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^{3}$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 2.6.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21\ atm$)?

Answer

$4.8 \times 10^{-31}\ atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 2.6.6.

Example 2.6.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).
C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 2.6.5. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[H_{2(g)}]$	$[C_2H_{4(g)}]$	$[C_2H_{6(g)}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	$+x$	$+x$	$-x$
Final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x)$ = 0.045 and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 2.6.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M\ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$



A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: Using ICE Tables to find Eq. Concentrations & Kc(opens in new window) [youtu.be]

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated

from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

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2.7: The Reaction Quotient- Predicting the Direction of Change

Learning Objectives

- To predict in which direction a reaction will proceed.

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a Quantity called the reaction Quotient (Q). The expression for the reaction Quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2.7.1}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} \tag{2.7.2}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table **2.7.1**: Equilibrium Experiment data

Experiment	$[\mathrm{NO_2}]$ (M)	$[\mathrm{N_2O_4}]$ (M)	$Q = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K:

- If $Q = K$, for example, then the system is already at equilibrium, and **no further change** in the composition of the system will occur unless the conditions are changed.
- If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the **right** as written, forming products at the expense of reactants.
- If $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the **left** as written, forming reactants at the expense of products.

These points are illustrated graphically in Figure 2.7.1.

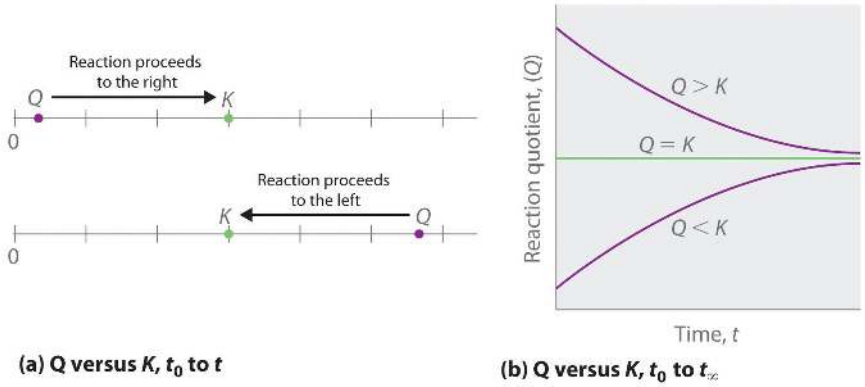


Figure 2.7.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

One way is used two number lines. The second way is to use a graph of reaction quotient against time.

> *If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.*



A Video Discussing Using the Reaction Quotient (Q): Using the Reaction Quotient (Q) (opens in new window) [youtu.be]

Example 2.7.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of

H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A. Calculate the molar concentrations of the reactants and the products.
B. Use Equation 2.7.1 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2}\,\text{mol}}{2.0\,\text{L}} = 6.0 \times 10^{-3} M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B We now compute Q and compare it with K:

$$\begin{aligned} Q &= \frac{[CO][H_2]^3}{[CH_4][H_2O]} \\ &= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

? Exercise 2.7.2

In the water–gas shift reaction introduced in Example 2.7.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

$Q = 0.96$. Since (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Reaction 1

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$\mathrm{PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)} \tag{2.7.3}$$

Because $\mathrm{PbCO_3}$ and PbO are solids, the equilibrium constant is simply

$$K = [\mathrm{CO_2}].$$

At a given temperature, therefore, any system that contains solid $\mathrm{PbCO_3}$ and solid PbO will have exactly the same concentration of $\mathrm{CO_2}$ at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 2.7.3, which shows a plot of $[\mathrm{CO_2}]$ versus the amount of $\mathrm{PbCO_3}$ added. Initially, the added $\mathrm{PbCO_3}$ decomposes completely to $\mathrm{CO_2}$ because the amount of $\mathrm{PbCO_3}$ is not sufficient to give a $\mathrm{CO_2}$ concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $\mathrm{CO_2(g)}$ and $\mathrm{PbO(s)}$. In contrast, when just enough $\mathrm{PbCO_3}$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $\mathrm{PbCO_3}$ has no effect on the $\mathrm{CO_2}$ concentration: the graph is a horizontal line.

Thus any $\mathrm{CO_2}$ concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $\mathrm{PbCO_3}$ and PbO are present. For example, the point labeled **A** in Figure 2.7.2 lies above the horizontal line, so it corresponds to a $[\mathrm{CO_2}]$ that is greater than the equilibrium concentration of $\mathrm{CO_2}$ (i.e., $Q > K$). To reach equilibrium, the system must decrease $[\mathrm{CO_2}]$, which it can do only by reacting $\mathrm{CO_2}$ with solid PbO to form solid $\mathrm{PbCO_3}$. Thus the reaction in Equation 2.7.3 will proceed to the left as written, until $[\mathrm{CO_2}] = K$. Conversely, the point labeled **B** in Figure 2.7.2 lies below the horizontal line, so it corresponds to a $[\mathrm{CO_2}]$ that is less than the equilibrium concentration of $\mathrm{CO_2}$ (i.e., $Q < K$). To reach equilibrium, the system must increase $[\mathrm{CO_2}]$, which it can do only by decomposing solid $\mathrm{PbCO_3}$ to form $\mathrm{CO_2}$ and solid PbO. The reaction in Equation 2.7.3 will therefore proceed to the right as written, until $[\mathrm{CO_2}] = K$.

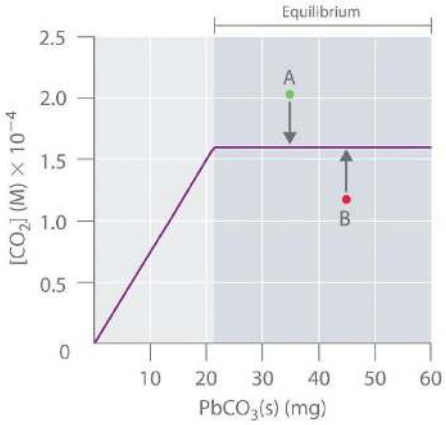


Figure 2.7.2: The Concentration of Gaseous $\mathrm{CO_2}$ in a Closed System at Equilibrium as a Function of the Amount of Solid $\mathrm{PbCO_3}$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $\mathrm{PbCO_3}$ added, as $\mathrm{PbCO_3}$ decomposes to $\mathrm{CO_2(g)}$ and solid PbO. Once the $\mathrm{CO_2}$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $\mathrm{PbCO_3}$ has no effect on $[\mathrm{CO_2}]$, as long as the temperature remains constant.

Reaction 2

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$\mathrm{CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g)} \tag{2.7.4}$$

and the equilibrium constant is

$$K = \frac{[\mathrm{H_2O}]}{[\mathrm{H_2}]}.$$

If $[\mathrm{H_2O}]$ is doubled at equilibrium, then $[\mathrm{H_2}]$ must also be doubled for the system to remain at equilibrium. A plot of $[\mathrm{H_2O}]$ versus $[\mathrm{H_2}]$ at equilibrium is a straight line with a slope of K (Figure 2.7.3). Again, only those pairs of concentrations of $\mathrm{H_2O}$ and $\mathrm{H_2}$ that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line

corresponds to a nonequilibrium state. In such cases, the reaction in Equation 2.7.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point **A** in Figure **2.7.3** lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (i.e., $Q < K$). Thus the reaction in Equation 2.7.4 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point **B** in Figure **2.7.3** lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 2.7.4 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

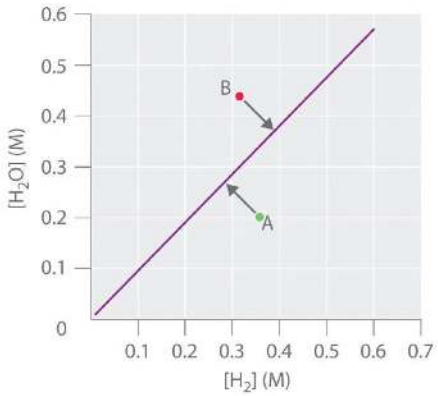


Figure **2.7.3**: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

Reaction 3

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I\,(s) \rightleftharpoons NH_3\,(g) + HI\,(g) \tag{2.7.5}$$

For this system, K is equal to the product of the concentrations of the two products:

$$K = [NH_3][HI].$$

If we double the concentration of NH_3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure **2.7.4**. As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which

$$[NH_3] = [HI] = \sqrt{K}.$$

Any point that lies below and to the left of the equilibrium curve (such as point **A** in Figure **2.7.4**) corresponds to $Q < K$, and the reaction in Equation 2.7.5 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point **B** in Figure 2.7.5) corresponds to $Q > K$, and the reaction in Equation 2.7.5 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

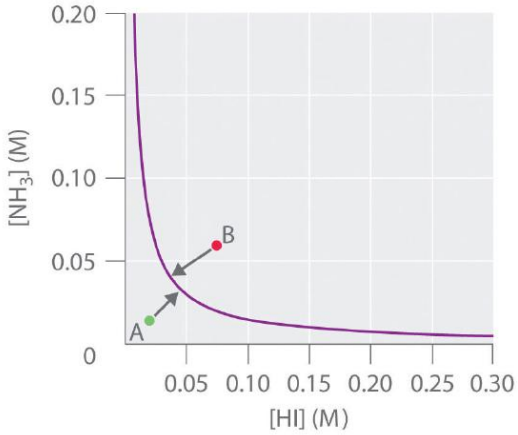


Figure 2.7.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for system in Reaction 2.7.5 at Equilibrium. Only one equilibrium concentration of $\mathrm{NH_3\,(g)}$ is possible for any given equilibrium concentration of $\mathrm{HI\,(g)}$. In this case, the two are inversely proportional. Thus a large $\mathrm{[HI]}$ at equilibrium requires a small $\mathrm{[NH_3]}$ at equilibrium and vice versa.

Summary

The reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. The reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

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2.8: Le Châtelier's Principle- How a System at Equilibrium Responds to Disturbances

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 ($Q \leq K$) or the reactants (if ($Q \geq K$) until Q returns to the same value as K. This process is described by Le Chatelier's principle.

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 **2.8.1** is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure **2.8.1**: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN. $\mathbf{Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)}$. The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)} \tag{2.8.1}$$

$$K_c = 50.0 \text{ at } 400^\circ\mathrm{C} \tag{2.8.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[\mathrm{H_2}] = [\mathrm{I_2}] = 0.221\ M$ and $[\mathrm{HI}] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If $\mathrm{H_2}$ is introduced into the system so quickly that its concentration doubles before it begins to react (new $[\mathrm{H_2}] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[\mathrm{H_2}] = 0.374\ M$,
- $[\mathrm{I_2}] = 0.153\ M$, and
- $[\mathrm{HI}] = 1.692\ M$.

This gives:

$$\begin{aligned} Q_c &= \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} \\ &= \frac{(1.692)^2}{(0.374)(0.153)} \\ &= 50.0 = K_c \end{aligned}$$

We have stressed this system by introducing additional $\mathrm{H_2}$. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess $\mathrm{H_2}$, reducing the amount of uncombined $\mathrm{I_2}$, and forming additional HI. **Le Chatelier's Principle (Changing Concentrations):** Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be]



A Video Discussing Le Chatelier's Principle (Changing Concentrations): Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be] (opens in new window)

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 $\mathbf{NO}$, $\mathbf{O_2}$, and $\mathbf{NO_2}$ are at equilibrium:

$$\mathbf{2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)} \tag{2.8.3}$$

The formation of additional amounts of $\mathbf{NO_2}$ decreases the total number of molecules in the system because each time two molecules of $\mathbf{NO_2}$ form, a total of three molecules of $\mathbf{NO}$ and $\mathbf{O_2}$ 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 $\mathbf{NO_2}$ into $\mathbf{NO}$ and $\mathbf{O_2}$, which tends to restore the pressure.

Now consider this reaction:

$$\mathbf{N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)} \tag{2.8.4}$$

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.



Le Chatelier’s Principle (Changes in Pressure or Volume):

Le Chatelier’s Principle (Changes in Pressure or Volume)(opens in new window) [youtu.be]

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.

$$\mathbf{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad \Delta H = -9.4\ \mathbf{kJ\ (exothermic)} \tag{2.8.5}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathbf{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) + heat} \tag{2.8.6}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between $\mathbf{NO_2}$ and $\mathbf{N_2O_4}$ in this reaction

$$\mathbf{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g) \quad \Delta \mathit{H} = 57.20\ kJ} \tag{2.8.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathbf{heat + N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)} \tag{2.8.8}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown $\mathbf{NO_2}$ 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 $\mathbf{N_2O_4}$ increases, and the concentration of brown $\mathbf{NO_2}$ decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table **2.8.1**.

Table **2.8.1**: Effects of Disturbances of Equilibrium and $\boldsymbol{K}$

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

Example 2.8.1

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

a. $\mathbf{2}\mathit{HgO}_{(s)} \rightleftharpoons \mathbf{2}\mathit{Hg}_{(l)} + \mathbf{O}_{2(g)}$: the amount of HgO is doubled.
b. $\mathit{NH_4HS}_{(s)} \rightleftharpoons \mathbf{NH_{3(g)}} + \mathit{H_2S}_{(g)}$: the concentration of $\mathit{H_2S}$ is tripled.
c. $\mathbf{n\text{-}butane}_{(g)} \rightleftharpoons \mathit{isobutane}_{(g)}$: the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

Because $HgO_{(s)}$ and $Hg_{(l)}$ are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2, so no compensatory change is necessary.

NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K.

For this reaction, $K = \frac{[isobutane]}{[n\text{-}butane]}$, so halving the concentration of isobutane means that the n-butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise 2.8.1

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

a. $\mathbf{HBr}(g) + \mathrm{NaH}(s) \rightleftharpoons \mathrm{NaBr}(s) + \mathbf{H_2}(g)$: the concentration of **HBr** is decreased by a factor of 3.
b. $6\,\mathrm{Li}(s) + \mathbf{N_2}(g) \rightleftharpoons 2\,\mathrm{Li_3N}(s)$: the amount of **Li** is tripled.
c. $\mathbf{SO_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{SO_2Cl_2}(l)$: the concentration of $\mathbf{Cl_2}$ is doubled.

Answer a

$K = \frac{[H_2]}{[HBr]}$; $[H_2]$ must decrease by about a factor of 3.

Answer b

$K = \frac{1}{[N_2]}$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.

Answer c

$K = \frac{1}{[SO_2][Cl_2]}$; $[SO_2]$ must decrease by about half.



Le Chatelier's Principle (Changes in Temperature):

Le Chatelier's Principle (Changes in Temperature)(opens in new window) [youtu.be]

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

$$\mathrm{N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)} \tag{2.8.9}$$

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. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements (Equation 2.8.9). 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.



Figure 2.8.1: 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.

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 to a majority of plants due the tremendous stability of the nitrogen-nitrogen triple bond. Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.

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.

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.

Footnotes

1. 1 Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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2.E: Chemical Equilibrium (Practice Problems with Answers)

15.1: The Concept of Equilibrium

Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the amounts or concentrations of the reactants and the products?
2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.
3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of $NaCl$ in water. What is occurring on a microscopic level? What is happening on a macroscopic level?
4. Which of these systems exists in a state of chemical equilibrium?
   a. oxygen and hemoglobin in the human circulatory system
   b. iodine crystals in an open beaker
   c. the combustion of wood
   d. the amount of ^{14}C in a decomposing organism

Conceptual Answer

1. When a reaction is described as "having reached equilibrium" this means that the forward reaction rate is now equal to the reverse reaction rate. In regards to the amounts or concentrations of the reactants and the products, there is no change due to the forward reaction rate being equal to the reverse reaction rate.

2. It is not correct to say that the reaction has "stopped" when it has reached equilibrium because it is not necessarily a static process where it can be assumed that the reaction rates cancel each other out to equal zero or be "stopped" but rather a dynamic process in which reactants are converted to products at the same rate products are converted to reactants. For example, a soda has carbon dioxide dissolved in the liquid and carbon dioxide between the liquid and the cap that is constantly being exchanged with each other. The system is in equilibrium and the reaction taking place is: $CO_2\,(g) + 2\,H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)$.

3. Chemical equilibrium is described as a dynamic process because there is a movement in which the forward and reverse reactions occur at the same rate to reach a point where the amounts or concentrations of the reactants and products are unchanging with time. Chemical equilibrium can be described in a saturated solution of $NaCl$ as on the microscopic level Na^+ and Cl^- ions continuously leave the surface of an $NaCl$ crystal to enter the solution, while at the same time Na^+ and Cl^- ions in solution precipitate on the surface of the crystal. At the macroscopic level, the salt can be seen to dissolve or not dissolve depending whether chemical equilibrium was established.

4.

a. Exists in a state of equilibrium as the chemical reaction that occurs in the body is: $Hb\,(aq) + 4\,H_2O\,(l) \rightleftharpoons Hb(O_2)_4\,(aq)$.

b. Exists in a state of equilibrium as the chemical reaction occurs is: $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$

c. Does not exist in a state of equilibrium as it is not a reversible process. The chemical reaction that takes place is: $C_{10}H_{15}O_7\,(s) + heat \rightarrow C_{50}H_{10}O\,(s) + 10\,CH_2O\,(g)$.

d. Does not exist in a state of chemical equilibrium as it is not a reversible process. The chemical reaction that takes place is: $CH_2O + O_2 \rightarrow H_2O\,(l) + CO_2\,(g) + nutrients$.

15.2: The Equilibrium Constant

Conceptual Problems

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?
2. Which of the following equilibriums are homogeneous and which are heterogeneous?
   a. $2\,HF\,(g) \rightleftharpoons H_2\,(g) + F_2\,(g)$

b. $C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$
c. $H_2C = CH_2(g) + H_2(g) \rightleftharpoons C_2H_6(g)$
d. $2\,Hg(l) + O_2(g) \rightleftharpoons 2\,HgO(s)$

3. Classify each equilibrium system as either homogeneous or heterogeneous.
   a. $NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
   b. $C(s) + O_2(g) \rightleftharpoons CO_2(g)$
   c. $2\,Mg(s) + O_2(g) \rightleftharpoons 2\,MgO(s)$
   d. $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
4. If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?
5. Industrial production of NO by the reaction $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ is carried out at elevated temperatures to drive the reaction toward the formation of the product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?
6. How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?
7. What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?
8. Write the equilibrium constant expressions for K and K_p for each reaction.
   a. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
   b. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
   c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
9. Write the equilibrium constant expressions for K and K_p as appropriate for each reaction.
   a. $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$
   b. $\frac{1}{2}\,H_2(g) + 12\,I_2(g) \rightleftharpoons HI(g)$
   c. $cis - stilbene(soln) \rightleftharpoons trans - silbene(soln)$
10. Why is it incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression?
11. Write the equilibrium constant expressions for K and K_p for each equilibrium reaction.
    a. $2\,S(s) + 3\,O_2(g) \rightleftharpoons 2\,SO_3(g)$
    b. $C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$
    c. $2\,ZnS(s) + 3\,O_2(g) \rightleftharpoons 2\,ZnO(s) + 2\,SO_2(g)$
12. Write the equilibrium constant expressions for K and K_p for each equilibrium reaction.
    a. $2\,HgO(s) \rightleftharpoons 2\,Hg(l) + O_2(g)$
    b. $H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$
    c. $NH_4CO_2NH_2(s) \rightleftharpoons 2\,NH_3(g) + CO_2(g)$
13. At room temperature, the equilibrium constant for the reaction $2\,A(g) \rightleftharpoons B(g)$ is 1. What does this indicate about the concentrations of A and B at equilibrium? Would you expect K and K_p to vary significantly from each other? If so, how would their difference be affected by temperature?
14. For a certain series of reactions, if $\frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = K_1$ and $\frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = K_2$, what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.
15. In the equation for an enzymatic reaction, ES represents the complex formed between the substrate S and the enzyme protein E. In the final step of the following oxidation reaction, the product P dissociates from the ESO_2 complex, which regenerates the active enzyme:

$$E + S \rightleftharpoons ES \quad K_1 \tag{2.E.1}$$

$$ES + O_2 \rightleftharpoons ESO_2 \quad K_2 \tag{2.E.2}$$

$$ESO_2 \rightleftharpoons E + P \quad K_3 \tag{2.E.3}$$

Give the overall reaction equation and show that $K = K_1 \times K_2 \times K_3$.

Conceptual Answers

1. By reversing the reactants and products for an equilibrium reaction, the equilibrium constant becomes: $K' = \frac{1}{K}$.

2.

a. This equilibrium is homogenous as all substances are in the same state.

b. This equilibrium is heterogeneous as not all substances are in the same state.

c. This equilibrium is homogeneous as all substances are in the same state.

d. This equilibrium is heterogeneous as not all substances are in the same state.

3.

a. This equilibrium is heterogeneous as not all substances are in the same state.

b. This equilibrium is heterogeneous as not all substances are in the same state.

c. This equilibrium is heterogeneous as not all substances are in the same state.

d. This equilibrium is heterogeneous as not all substances are in the same state.

4. According to Le Chatelier's principle, equilibrium will shift in the direction to counteract the effect of a constraint (such as concentration of a reactant, pressure, and temperature). Thus, in an endothermic reaction, the equilibrium shifts to the right-hand side when the temperature is increased which increases the equilibrium constant and the equilibrium shifts to the left-hand side when the temperature is decreased which decreases the equilibrium constant.

5. After sufficient industrial production of NO by the reaction of $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$ at elevated temperatures to drive the reaction toward the formation of the product, the reaction mixture is cooled quickly because it quenches the reaction and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.

6. To differentiate between a system that has reached equilibrium and one that is reacting slowly that changes in concentrations are difficult to observe we can use Le Chatelier's principle to observe any shifts in the reaction upon addition of a constraint (such as concentration, pressure, or temperature).

7. The relationship between the equilibrium constant, the concentration of each component of a system, and the rate constants for the forward and reverse reactions considering a reaction of a general form: $a\,A + b\,B \rightleftharpoons c\,C + d\,D$ is $K = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{k_f}{k_r}$

8.

a.

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})}$$

b.

$$K = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

$$K_p = \frac{(P_{PCl_5})}{(P_{Cl_3})(P_{Cl_2})}$$

c.

$$K = \frac{[O_2]^3}{[O_3]^2}$$

$$K_p = \frac{(P_{O_2})^3}{(P_{O_3})^2}$$

9.

a.

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{NO})^2(P_{O_2})}$$

b.

$$K = \frac{[HI]}{[H_2]^{\frac{1}{2}}[O_2]}$$

$$K_p = \frac{(P_{HI})}{(P_{H_2})^{\frac{1}{2}}(P_{O_2})}$$

c.

$$K = \frac{trans - stilbene}{cis - stilbene}$$

$$K_p = \frac{(P_{trans-stilbene})}{(P_{cis-stilbene})}$$

10. It is incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression because they are not reactive enough or cause a change in the concentrations of the ions or the species that exist in the gas phase.

11.

a.

$$K = \frac{[SO_3]^2}{[O_2]^3}$$

$$K_p = \frac{(P_{SO_3})^2}{(P_{O_2})^3}$$

b.

$$K = \frac{[CO]^2}{[CO_2]}$$

$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})}$$

c.

$$K = \frac{[SO_2]^2}{[O_2]^3}$$

$$K_p = \frac{(P_{SO_2})^2}{(P_{O_2})^3}$$

12.

a.

$$K = [O_2]$$

$$K_p = (P_{O_2})$$

b.

$$K = \frac{[HI]^2}{[H_2]}$$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})}$$

c.

$$K = [NH_3]^2[CO_2]$$

$K_p = (P_{NH_3})^2(P_{CO_2})$

13.

$K = \frac{[B]}{[A]^2} \rightarrow 1 = \frac{[B]}{[A]^2} \rightarrow [A]^2 = [B] \rightarrow [A] = \sqrt{B}$

K and K_p vary by RT, but it largely depends on T as R is constant. A raise or decrease in temperature would cause a difference.

$$K_p = K(RT)^{\Delta n} = K(RT)^{-1} = \frac{K}{RT}$$

$$\Delta n = (\text{total moles of gas on the product side}) - (\text{total of moles on the reactant side}) = 1 - 2 = -1$$

14.

$$K = \frac{K_1}{K_2} = \frac{\frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]}}{\frac{[OH^-][H_2CO_3]}{[HCO_3^-]}} = \frac{[HCO_3^-]^2}{[CO_3^{2-}][H_2CO_3]}$$

$CO_3^{2-}(g) + H_2CO_3(g) \rightleftharpoons 2\,HCO_3^-(g)$

15.

$K = K_1 \times K_2 \times K_3 = \frac{[ES]}{[E][S]} \times \frac{[ESO_2]}{[ES][O_2]} \times \frac{[E][P]}{[ESO_2]} = \frac{[P]}{[S][O_2]}$

$S + O_2 \rightleftharpoons P$

Numerical Problems

1. Explain what each of the following values for K tells you about the relative concentrations of the reactants versus the products in a given equilibrium reaction: $K = 0.892$; $K = 3.25 \times 10^8$; $K = 5.26 \times 10^{-11}$. Are products or reactants favored at equilibrium?
2. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.
   a. $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$
   b. $\frac{1}{2}\,N_2O_4(g) \rightleftharpoons NO_2(g)$
3. Write the equilibrium constant expression for each reaction.
   a. $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$
   b. $\frac{1}{3}N_2(g) + H_2(g) \rightleftharpoons \frac{2}{3}NH_3(g)$

How are these two expressions mathematically related to the equilibrium constant expression for

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)? \qquad (2.E.4)$$

4. Write an equilibrium constant expression for each reaction.
   a. $C(s) + 2\,H_2O(g) \rightleftharpoons CO_2(g) + 2\,H_2(g)$
   b. $SbCl_3(g) + Cl_2(g) \rightleftharpoons SbCl_5(g)$
   c. $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
5. Give an equilibrium constant expression for each reaction.

a. $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$

b. $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$

c. $CaCO_3(s) + 2\,HOCl(aq) \rightleftharpoons Ca^{2+}(aq) + 2\,OCl^-(aq) + H_2O(l) + CO_2(g)$

6. Calculate K and K_p for each reaction.
   a. $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$: at 727°C, the equilibrium concentration of NO is 1.29 M, Br_2 is 10.52 M, and $NOBr$ is 0.423 M.
   b. $C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$: at 1,200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm CO_2 and 76.8 atm CO, and the vessel contains 3.55 g of carbon.
7. Calculate K and K_p for each reaction.

a. $N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$: at the equilibrium temperature of −40°C, a 0.150 M sample of N_2O_4 undergoes a decomposition of 0.456%.
b. $CO\,(g) + 2\,H_2\,(g) \rightleftharpoons CH_3OH\,(g)$: an equilibrium is reached at 227°C in a 15.5 L reaction vessel with a total pressure of 6.71×10^2 atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7,193 g of methanol.

8. Determine K and K_p (where applicable) for each reaction.

a. $2\,H_2S\,(g) \rightleftharpoons 2\,H_2\,(g) + S_2\,(g)$: at 1065°C, an equilibrium mixture consists of 1.00×10^{-3} M H_2, 1.20×10^{-3} M S_2, and 3.32×10^{-3} M H_2S.
b. $Ba(OH)_2\,(s) \rightleftharpoons 2\,OH^-\,(aq) + Ba^{2+}\,(aq)$: at 25°C, a 250 mL beaker contains 0.330 mol of barium hydroxide in equilibrium with 0.0267 mol of barium ions and 0.0534 mol of hydroxide ions.

9. Determine K and K_p for each reaction.

a. $2\,NOCl\,(g) \rightleftharpoons 2\,NO\,(g) + Cl_2\,(g)$: at 500 K, a 24.3 mM sample of $NOCl$ has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of $NOCl$.
b. $Cl_2\,(g) + PCl_3\,(g) \rightleftharpoons PCl_5\,(g)$: at 250°C, a 500 mL reaction vessel contains 16.9 g of Cl_2 gas, 0.500 g of PCl_3, and 10.2 g of PCl_5 at equilibrium.

10. The equilibrium constant expression for a reaction is $\frac{[CO_2]^2}{[SO_2]^2[O_2]}$. What is the balanced chemical equation for the overall reaction if one of the reactants is $Na_2CO_3\,(s)$?

11. The equilibrium constant expression for a reaction is $\frac{[NO][H_2O]^{\frac{3}{2}}}{[NH_3][O_2]^{\frac{5}{4}}}$. What is the balanced chemical equation for the overall reaction?

12. Given $K = \frac{k_f}{k_r}$, what happens to the magnitude of the equilibrium constant if the reaction rate of the forward reaction is doubled? What happens if the reaction rate of the reverse reaction for the overall reaction is decreased by a factor of 3?

13. The value of the equilibrium constant for

$$2\,H_2\,(g) + S_2\,(g) \rightleftharpoons 2\,H_2S\,(g) \tag{2.E.5}$$

is 1.08×10^7 at 700°C. What is the value of the equilibrium constant for the following related reactions

a. $H_2\,(g) + 12\,S_2\,(g) \rightleftharpoons H_2S\,(g)$
b. $4\,H_2\,(g) + 2\,S_2\,(g) \rightleftharpoons 4\,H_2S\,(g)$
c. $H_2S\,(g) \rightleftharpoons H_2\,(g) + 12\,S_2\,(g)$

Numerical Answers

1. In the given equilibrium reaction where $K = 0.892 \approx 1$ has a concentration of the reactants that is approximately equal to the concentration of the products so neither formation of the reactants or products is favored. In the given equilibrium reaction where $K = 3.25 \times 10^8 > 1$ has a concentration of the products that is relatively small compared to the concentration of the reactants so the formation of the products is favored. In the given equilibrium reaction where $K = 5.26 \times 10^{-11} < 1$ has a concentration of products that is relatively large compared to that of the concentration of the reactants so the formation of the reactants is favored.

2.

a. $K = \frac{[NO_2]^2}{[N_2O_4]}$

b. $K = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}}$

Although the equilibrium constant expressions have a 2:1 ratio of concentration for the products to the concentration of the reactants for the same species involved to get the K value for a. We would need to square it to get the K value for b.

3.

a. $K' = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$

b. $K'' = \frac{[NH_3]^{\frac{2}{3}}}{[N_2]^{\frac{1}{2}}[H_2]}$

$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$K' = K^{\frac{1}{2}}$

$K'' = K^{\frac{1}{3}}$

4.

a. $K = \frac{[H_2]^2[CO_2]}{[H_2O]^2}$

b. $K = \frac{[SbCl_5]}{[SbCl_3][Cl_2]}$

c. $K = \frac{[O_2]^3}{[O_3]^2}$

5.

a. $K = \frac{[NO_2]^2}{[NO]^2[O_2]}$

b. $K = \frac{[HI]}{[H_2]^{\frac{1}{2}}[I_2]^{\frac{1}{2}}}$

c. $K = \frac{[Ca^{2+}][OCl^-]^2[CO_2]}{[HOCl]^2}$

6.

a.

$K = \frac{[NO]^2[Br]}{[NOBr]^2} = \frac{[1.29\ M]^2[10.52\ M]}{[0.423\ M]^2} = 97.8$

$K_p = K(RT)^{\Delta n} = (97.8)((0.08206\frac{L \cdot atm}{mol \cdot K})((727 + 273.15)K))^{3-2} = 8.03x10^4$

b.

$K_p = K(RT)^{\Delta n} = K(RT)^{2-1} = K(RT) \rightarrow K = \frac{K_p}{RT} = \frac{63.1}{(0.08206\frac{L \cdot atm}{mol \cdot K})(1{,}200\ K)} = 6.41$

$K = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(76.8\ atm)^2}{93.5\ atm} = 63.1$

7.

a.

$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.001368\ M]}{[0.149316\ M]} = 1.25x10^{-5}$

$[NO_2] = (2)(0.150\ M)(0.00456) = 0.001368\ M$

$[N_2O_4] = (0.150\ M)(1 - 0.00456) = 0.149316\ M$

$K_p = K(RT)^{\Delta n} = (1.25x10^{-5})((0.08206\frac{L \cdot atm}{mol \cdot K})((-40 + 273.15)K))^{2-1} = 2.39x10^{-4}$

b.

$K = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{[14.5\ M]}{[1.05\ M][1.21\ M]^2} = 9.47$

$$[CH_3OH] = 7,193\,g\,CH_3OH \times \frac{1\,mol\,CH_3OH}{32.04\,g\,CH_3OH} \times \frac{1}{15.5\,L} = 14.5\,M$$

$$[CO] = 457.7\,g\,CO \times \frac{1\,mol\,CO}{28.01\,g\,CO} \times \frac{1}{15.5\,L} = 1.05\,M$$

$$[H_2] = 37.8\,g\,H_2 \times \frac{1\,mol\,H_2}{2.02\,g\,H_2} \times \frac{1}{15.5\,L} = 1.21\,M$$

$K_p = K(RT)^{\Delta n} = (9.47)((0.08206\frac{L{\cdot}atm}{mol{\cdot}K})((227 + 273.15)K))^{1-3} = 5.62x10^{-2}$

8.

a.

$K = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{[1.00\times10^{-3}\,M]^2[1.20\times10^{-3}\,M]}{[3.32\times\,10^{-3}\,M]^2} = 1.09 \times 10^{-4}$

$K_p = K(RT)^{\Delta n} = (1.09 \times 10^{-4})((0.08206\frac{L{\cdot}atm}{mol{\cdot}K})((1065 + 273.15)K))^{3-2} = 1.20 \times 10^{-2}$

b.

$K = [OH^-]^2[Ba^{2+}] = [0.2136\,M]^2[0.1068\,M] = 4.87 \times 10^{-3}$

$$[OH^-] = 0.0534\,mol\,OH^- \times \frac{1}{0.25\,L} = 0.2136\,M$$

$$[Ba^{2+}] = 0.0267\,mol\,Ba^{2+} \times \frac{1}{0.25\,L} = 0.1068\,M$$

$K_p = K(RT)^{\Delta n} = (4.87 \times 10^{-3})((0.08206\frac{L{\cdot}atm}{mol{\cdot}K})((25 + 273.15)K))^{3-1} = 2.92$

9.

a.

$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = 4.59 \times 10^{-4}$

$K_p = K(RT)^{\Delta n} = (4.59 \times 10^{-4})((0.08206\frac{L{\cdot}atm}{mol{\cdot}K})(500K))^{3-2} = 1.88 \times 10^{-2}$

b.

$K = \frac{[PCl_5]}{[Cl_2][PCl_3]} = \frac{[9.80\times10^{-2}\,M]}{[4.77\times10^{-1}\,M][7.28\times10^{-3}\,M]} = 28.2$

$$[PCl_5] = 10.2\,g\,PCl_5 \times \frac{1\,mol\,PCl_5}{208.2388\,g\,PCl_5} \times \frac{1}{0.5\,L} = 9.80 \times 10^{-2}\,M$$

$$[Cl_2] = 16.9\,g\,Cl_2 \times \frac{1\,mol\,Cl_2}{70.9\,g\,Cl_2} \times \frac{1}{0.5\,L} = 4.77 \times 10^{-1}\,M$$

$$[PCl_3] = 0.500\,g\,PCl_3 \times \frac{1\,mol\,PCl_3}{137.33\,g\,PCl_3} \times \frac{1}{0.5\,L} = 7.28 \times 10^{-3}\,M$$

$K_p = K(RT)^{\Delta n} = (28.2)((0.08206\frac{L{\cdot}atm}{mol{\cdot}K})(250 + 273.15)K)^{1-2} = 6.57 \times 10^{-1}$

10. $2\,SO_2\,(g) + O_2\,(g) + 2\,Na_2CO_3\,(s) \rightleftharpoons 2\,CO_2\,(g) + 2\,Na_2SO_4\,(s)$

11. $NH_3\,(g) + \frac{5}{4}\,O_2\,(g) \rightleftharpoons NO\,(g) + \frac{3}{2}\,H_2O\,(g)$

12. If the reaction rate of the forward reaction is doubled the magnitude of the equilibrium constant is doubled. If the reaction rate of the reverse reaction for the overall reaction is described by a factor of 3 the magnitude of the equilibrium constant is increased by a factor of 3.

13. $K' = \frac{[H_2S]^2}{[H_2]^2[S_2]} = 1.08 \times 10^7$

a. $K = \frac{[H_2S]}{[H_2][S_2]^{\frac{1}{2}}} = K'^{\frac{1}{2}} = (1.08 \times 10^7)^{\frac{1}{2}} = 3.29 \times 10^3$ b. $K = \frac{[H_2S]^4}{[H_2]^4[S_2]^2} = K'^2 = (1.08 \times 10^7)^2 = 1.17 \times 10^{14}$ c. $K = \frac{[H_2][S_2]^{\frac{1}{2}}}{[H_2S]} = K'^{-\frac{1}{2}} = (1.08 \times 10^7)^{-\frac{1}{2}} = 3.04 \times 10^{-4}$

15.3: Interpreting & Working with Equilibrium Constants

Conceptual Problems

1. Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.

2. Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making certain assumptions about the concentrations of products and reactants. What are these assumptions when K is (a) very large and (b) very small? Illustrate this technique using the system $A + 2B \rightleftharpoons C$ for which you are to calculate the concentration of the product at equilibrium starting with only A and B. Under what circumstances should simplifying assumptions not be used?

Conceptual Answers

1. The magnitude of the equilibrium constant for a reaction depends on the form in which the chemical reaction is written. For example, writing a chemical reaction in different but chemically equivalent forms causes the magnitude of the equilibrium constant to be different but can be related by comparing their respective magnitudes.

2.

a. When K is very large the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion.

$$K = \frac{[C]}{[A][B]^2} = \frac{[C]}{very\ small} = \frac{1}{0} = \infty \rightarrow [C] = \infty$$

b. When K is very small the reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of the reactants.

$$K = \frac{[C]}{[A][B]^2} = \frac{very\ small}{[A][B]^2} = \frac{0}{1} = 0 \rightarrow [C] = 0$$

Simplifying assumptions should not be used if the equilibrium constant is not known to be very large or very small.

Numerical Problems

Please be sure you are familiar with the quadratic formula before proceeding to the Numerical Problems.

1. In the equilibrium reaction $A + B \rightleftharpoons C$, what happens to K if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction $2\,A \rightleftharpoons B + C$?
2. The following table shows the reported values of the equilibrium P_{O_2} at three temperatures for the reaction $Ag_2O\,(s) \rightleftharpoons 2\,Ag\,(s) + \frac{1}{2}\,O_2\,(g)$, for which ΔH° = 31 kJ/mol. Are these data consistent with what you would expect to occur? Why or why not?

T (°C)	$P_{O_2}\ (mmHg)$
150	182
184	143
191	126

3. Given the equilibrium system $N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$, what happens to K_p if the initial pressure of N_2O_4 is doubled? If K_p is 1.7×10^{-1} at 2300°C, and the system initially contains 100% N_2O_4 at a pressure of 2.6×10^2 atm, what is the equilibrium pressure of each component?
4. At 430°C, 4.20 mol of HI in a 9.60 L reaction vessel reaches equilibrium according to the following equation:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g) \tag{2.E.6}$$

   At equilibrium, $[H_2] = 0.047\ M$ and $[HI] = 0.345\ M$ What are K and K_p for this reaction?
5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction:

$$CO\,(g) + 2\,H_2\,(g) \rightleftharpoons CH_3OH\,(g) \tag{2.E.7}$$

   with $K_p = 1.3 \times 10^{-4}$. If 56.0 g of CO is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 atm, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?
6. Starting with pure A, if the total equilibrium pressure is 0.969 atm for the reaction $A\,(s) \rightleftharpoons 2\,B\,(g) + C\,(g)$, what is K_p?

7. The decomposition of ammonium carbamate to NH_3 and CO_2 at 40°C is written as $NH_4CO_2NH_2\,(s) \rightleftharpoons 2\,NH_3\,(g) + CO_2\,(g)$. If the partial pressure of NH_3 at equilibrium is 0.242 atm, what is the equilibrium partial pressure of CO_2? What is the total gas pressure of the system? What is K_p?
8. At 375 K, K_p for the reaction $SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$ is 2.4, with pressures expressed in atmospheres. At 303 K, K_p is 2.9×10^{-2}.
    a. What is K for the reaction at each temperature?
    b. If a sample at 375 K has 0.100 M Cl_2 and 0.200 M SO_2 at equilibrium, what is the concentration of SO_2Cl_2?
    c. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb?
9. For the gas-phase reaction $a\,A \rightleftharpoons b\,B$, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.
10. For the gas-phase reaction $I_2 \rightleftharpoons 2\,I$, show that the total pressure is related to the equilibrium pressure by the following equation:

$$P_T = \sqrt{K_p P_{I_2}} + P_{I_2} \tag{2.E.8}$$

11. Experimental data on the system $Br_2\,(l) \rightleftharpoons Br_2\,(aq)$ are given in the following table. Graph $Br_2\,(aq)$ versus moles of $Br_2\,(l)$ present; then write the equilibrium constant expression and determine K.

Grams Br_2 in 100 mL Water	Br_2 (M)
1.0	0.0626
2.5	0.156
3.0	0.188
4.0	0.219
4.5	0.219

12. Data accumulated for the reaction (\n-butane(g) \rightleftharpoons isobutane(g)\) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of n-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of n-butane and isobutane?

Moles n-butane	Moles Isobutane
0.5	1.25
1.0	2.5
1.50	3.75

13. Solid ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes: $NH_4CO_2NH_2\,(s) \rightleftharpoons 2\,NH_3\,(g) + CO_2\,(g)$ At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas? What is K_p? If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure +x atm, what change in the NH_3 concentration is necessary for the system to restore equilibrium?
14. The equilibrium constant for the reaction $COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g)$ is $K_p = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $COCl_2$ is $3.05 \times 10^{-3}\ M$, what is the partial pressure of each gas at equilibrium at 100°C? What assumption can be made to simplify your calculations?
15. Aqueous dilution of IO_4^- results in the following reaction:

$$IO_4^-\,(aq) + 2\,H_2O_{(l)} \rightleftharpoons H_4IO_6^-\,(aq) \tag{2.E.9}$$

with $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution of IO_4^- that is diluted to 250 mL with water, how many moles of $H_4IO_6^-$ are formed at equilibrium?
16. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation:

$$I_2\,(g) + Br_2\,(g) \rightleftharpoons 2\,IBr\,(g) \tag{2.E.10}$$

with $K_p = 1.2 \times 10^2$. If you begin the reaction with 7.4 g of I_2 vapor and 6.3 g of Br_2 vapor in a 1.00 L container, what is the concentration of $IBr\,(g)$ at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?

17. For the reaction

$$2\,C\,(s) + N_2\,(g) + 5\,H_2 \rightleftharpoons 2\,CH_3NH_2\,(g) \tag{2.E.11}$$

with $K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0 mol of N_2, 2.0 mol of H_2, and sufficient $C\,(s)$ in a 2.00 L container, what are the concentrations of N_2 and CH_3NH_2 at equilibrium? What happens to K if the concentration of H_2 is doubled?

Numerical Answers

1. In both cases, the equilibrium constant will remain the same as it does not depend on the concentrations.

2. No, the data is not consistent with what I would expect to occur because enthalpy is positive indicating that the reaction is endothermic thus heat is on the left side of the reaction. As the temperature is raised P_{O_2} would be expected to increase to counteract the constraint.

3.

If the initial pressure of N_2O_4 was doubled then K_p is one half of the original value.

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} \rightarrow 1.7 \times 10^{-1} = \frac{(2x)^2}{2.6\times10^2 - x} \rightarrow 44.2 - 0.17x = 4x^2 \rightarrow x \approx 3.303\,atm$$

	$P_{N_2O_4}$	P_{NO_2}
I	2.6×10^2	0
C	-x	+2x
E	$2.6 \times 10^2 - x$	2x

$P_{N_2O_4} = 2.6 \times 10^2 - x = 260 - 3.303 = 2.6 \times 10^2\,atm$

$P_{NO_2} = 2x = (2)(3.303) = 6.6\,atm$

4.

$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.345\,M}{(0.047\,M)(0.047\,M)} = 157$

$K_p = K(RT)^{\Delta n} = (157)((0.08206\frac{L\cdot atm}{mol\cdot K})(430 + 273.15)K)^{2-2} = 157$

5.

$Maximum\ Percent\ Yield = \frac{Actual}{Theoretical} \times 100\% = \frac{212.593}{376.127} \times 100\% = 56.52\% \approx 57\%$

$PV = nRT \rightarrow P = \frac{(1.999\ mol)(0.08206\frac{L\cdot atm}{mol\cdot K})(300+273.15)K}{0.250\ L} = 376.127\ atm$

$[CO] = 56.0\ g\ CO \times \frac{1\ mol\ CO}{28.01\ g\ CO} = 1.999\,mol\,CO$

$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{x}{(376.02-x)(100^2)} \rightarrow 1.3 = \frac{x}{376.07-x} \rightarrow 488.965 - 1.3x = x \rightarrow 488.965 = 2.3x \rightarrow x = 212.593\,atm$

$K_p = \frac{(P_{CH_3OH})}{(P_{CO})(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{357.320}{(376.127-357.320)(P_{H_2})^2} \rightarrow 1.3 \times 10^{-4} = \frac{357.320}{(18.80635)(P_{H_2})^2} \rightarrow 0.002444(P_{H_2})^2 = 357.320 \rightarrow (P_{H_2}) = 382.300 \approx 3.8 \times 10^2\,atm$

$Minimum\ Percent\ Yield = \frac{Actual}{Theoretical} \times 100\% \rightarrow 95\% = \frac{x}{376.127} \times 100\% \rightarrow x = 357.320\,atm$

	CO	$2\,H_2$	CH_3OH
I	376.127	100	0
C	-x	-2x	+x
E	376.127-x	100 (maintained)	x

6. $K_p = \frac{(P_B)^2(P_C)}{P_A} = \frac{[2x]^2[x]}{[0.969-x]} = \frac{4x^3}{0.969-x}$

	A	$2\,B$	C
I	0.969	0	0
C	-x	+2x	+x
E	0.969-x	2x	x

7.

$P_{CO_2} = P_{tot} - P_{NH_3} = P_{tot} - 0.242\,atm$

$P_{tot} = P_{NH_3} + P_{CO_2} = 0.242\,atm + P_{CO_2}$

$K_p = (P_{NH_3})^2(P_{CO_2}) = (0.242\,atm)^2(P_{CO_2})$

8.

a.

$At\,375\,K: K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.9\times10^{-2}}{((0.08206\frac{L\cdot atm}{mol\cdot K})(375\,K))^{2-1}} = 7.80\times10^{-2}$

$At\,303\,K: K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{2.9\times10^{-2}}{((0.08206\frac{L\cdot atm}{mol\cdot K})(303\,K))^{2-1}} = 1.17\times10^{-3}$

b. $K = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} \rightarrow [SO_2Cl_2] = \frac{[0.200\,M][0.100\,M]}{7.80\times10^{-2}} = 2.56\times10^{-1}\,M$

c. If the sample given in part b is cooled to 303 K, the pressure inside the bulb would decrease.

9.

$K_p = \frac{(P_B)^b}{(P_A)^a} = \frac{((\frac{n_B}{V})(RT))^b}{((\frac{n_A}{V})(RT))^a} = \frac{[B]^b(RT)^b}{[A]^a(RT)^a} = K(RT)^{b-a} = K(RT)^{\Delta n}$

$PV = nRT \rightarrow P = \frac{n}{V}RT$

$K = \frac{[B]^b}{[A]^a}$

$\Delta n = b - a$

10.

$P_T = P_I + P_{I_2} = \sqrt{K_p P_{I_2}} + P_{I_2}$

$K_p = \frac{(P_I)^2}{P_{I_2}} \rightarrow (P_I)^2 = K_p(P_{I_2}) \rightarrow P_I = \sqrt{K_p P_{I_2}}$

11.

The graph should be a positive linear correlation.

$Br_2\,(l)\,(M)\,(x-axis)$	$Br_2\,(aq)\,(M)\,(y-axis)\,(same\ value\ for\ K)$
6.26×10^{-2}	0.0626
1.56×10^{-1}	0.156
1.88×10^{-2}	0.188
2.50×10^{-2}	0.219
2.82×10^{-2}	0.219

$$[Br_2\,(l)] = 1.0\,g\,Br_2 \times \frac{1\,mol\,Br_2}{159.808\,g\,Br_2} \times \frac{1}{0.1\,L} = 6.26\times10^{-2}$$

$K = \frac{[Br_2\,(aq)]}{[Br_2\,(l)]} = \frac{[Br_2\,(aq)]}{1} = [Br_2\,(aq)]$

12. $K = \frac{[isobutane]}{[n-butane]} = \frac{x}{1-x}$

	$n-butane$	$isobutane$
I	1	0
C	-x	+x
E	1-x	x

13.

$P_{NH_3} = 2x = 2(0.0387) = 7.73\times10^{-2}\,atm$

$P_{CO_2} = x = 3.87\times10^{-2}\,atm$

$K_p = (P_{NH_3})^2(P_{CO_2}) = (2x)^2(x) = 4x^3 = 4(0.0387)^3 = 2.32\times10^{-4}$

$$P_{tot} = P_{NH_3} + P_{CO_2} \rightarrow 0.116 = 2x + x \rightarrow 0.116 = 3x \rightarrow x = 0.0387$$

If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure +x atm, the concentration of NH_3 should also be doubled for the system to restore equilibrium.

	NH_3	CO_2
I	0	0
C	2x	x
E	2x	x

14.

$P_{COCl_2} = 9.34\times10^{-2} - x = 9.34\times10^{-2} - 9.34\times10^{-22} = 9.34\times10^{-2}\,atm$

$P_{CO} = x = 9.34\times10^{-22}\,atm$

$P_{Cl_2} = x = 9.34\times10^{-22}\,atm$

Assume that the equilibrium mainly lies on the reactants side because the K_p value is less than 1.

$$K_p = \frac{(P_{CO})(P_{Cl_2})}{(P_{COCl_2})} \rightarrow 2.2\times10^{-10} = \frac{x^2}{9.34\times10^{-2}-x} \rightarrow 2.0548\times10^{-11} - 2.2\times10^{-10}x = x^2 \rightarrow x^2 + 2.2\times10^{-10}x - 2.0548\times10^{-11} = 0 \rightarrow x = 9.34\times10^{-22}$$

$$PV = nRT \rightarrow P = \frac{nRT}{V} = (3.05\times10^{-3})(0.08206\,\frac{L\cdot atm}{mol\cdot K})(100+273.15)K = 9.34\times10^{-2}$$

	$COCl_2$	CO	Cl_2
I	9.34×10^{-2}	0	0
C	-x	+x	+x
E	$9.34 \times 10^{-2} - x$	x	x

15. $[H_4IO_6^-] = x = 1.6 \times 10^{-3}\, mol$

$K = \frac{[H_4IO_6^-]}{[IO_4^-]} \rightarrow 3.5 \times 10^{-2} = \frac{x}{(0.0448-x)} \rightarrow x = 1.568 \times 10^{-3}$

$IO_4^- : 50\, mL\, IO_4^- \times \frac{1\, L\, IO_4^-}{1{,}000\, mL\, IO_4^-} \times \frac{0.896\, mol\, IO_4^-}{1\, L\, IO_4^-} = 0.0448\, mol$

	IO_4^-	$H_4IO_6^-$
I	0.0448	0
C	-x	+x
E	0.0448-x	x

16. $PV = nRT \rightarrow \frac{P}{RT} = \frac{n}{V} \rightarrow \frac{12.9468}{(0.08206 \frac{L \cdot atm}{mol \cdot K})(184.4+273.15)K} = 3.5 \times 10^{-1}\, M$

$K_p = \frac{(P_{IBr})^2}{(P_{I_2})(P_{Br_2})} \rightarrow 1.2 \times 10^{-2} = \frac{2x}{(1.096-x)(1.479-x)} = \frac{2x}{x^2-2.575x+1.62098} \rightarrow 0.012x^2 - 0.0309x + 0.0194518 = 2x \rightarrow 0.012x^2 - 2.0309 + 0.0194518 = 0 \rightarrow x = 12.9468$

	I_2	Br_2	IBr
I	1.096	1.479	0
C	-x	-x	2x
E	1.096-x	1.479-x	2x

$PV = nRT \rightarrow P = \frac{nRT}{V} = (2.92 \times 10^{-2}\, M)(0.08206 \frac{L \cdot atm}{mol \cdot K})(184.4 + 273.15)K = 1.096\, atm$

$[I_2] = 7.4\, g\, I_2 \times \frac{1\, mol\, I_2}{253\, g\, I_2} \times \frac{1}{1.00\, L} = 2.92 \times 10^{-2}\, M$

$PV = nRT \rightarrow P = nRTV = (3.94 \times 10^{-2}\, M)(0.08206 \frac{L \cdot atm}{mol \cdot K})(184.4 + 273.15)K = 1.479\, atm$

$[Br_2] = 6.3\, g\, Br_2 \times \frac{1\, mol\, Br_2}{159.808\, g\, Br_2} = 3.94 \times 10^{-2}\, M$

17.

$[N_2] = 0.5 - 12x = 0.5 - 12(0.000471330) = 0.494\, M$

$[CH_3NH_2] = 2x = 2(0.0004713300 = 9.43 \times 10^{-4}\, M$

$If\, the\, concentration\, of\, H_2\, is\, doubled\, ,\, then\, K = \frac{[CH_3NH_2]^2}{[N_2][H_2]^5} = \frac{(9.43 \times 10^{-4})^2}{(0.494)(1.998)^5} = 5.65 \times 10^{-8}$

$2 \times [H_2] = 2(1.0 - 2.5x) = 2(1.0 - 2.5(0.000471330)) = 1.998\, M$

$K = \frac{[CH_3NH_2]^2}{[N_2][H_2]^5} \rightarrow 1.8 \times 10^{-6} = \frac{(2x)^2}{(0.5-x)(1.0-5x)^5} \rightarrow x = 0.000471330\, M$

	C	N_2	H_2	CH_3NH_2
I	-	0.5	1.0	0
C	-	-x	-5x	2x
E	-	0.5-x	1.0-5x	2x

$[N_2] = 1.00\,mol\,N_2 \times \frac{1}{2.00\,L} = 0.5\,M$

$[H_2] = 2.00\,mol\,H_2 \times \frac{1}{2.00\,L} = 1.0\,M$

15.4: Heterogeneous Equilibria

15.5: Calculating Equilibrium Constants

15.6: Applications of Equilibrium Constants

Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 15.8 and Figure 15.9 as your guides, sketch the shape of each graph using appropriate labels.

a. $H_2O\,(l) \rightleftharpoons H_2O\,(g)$
b. $2\,MgO\,(s) \rightleftharpoons 2\,Mg\,(s) + O_2\,(g)$
c. $2\,O_3\,(g) \rightleftharpoons 3\,O_2\,(g)$
d. $2\,PbS\,(g) + 3\,O_2\,(g) \rightleftharpoons 2\,PbO\,(s) + 2\,SO_2\,(g)$

2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

a. $2\,NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g)$: $[CO_2]$ is doubled.
b. $N_2F_4\,(g) \rightleftharpoons 2\,NF_2\,(g)$: $[NF_2]$ is decreased by a factor of 2.
c. $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$: $[I_2]$ is doubled.

3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

a. $CS_2\,(g) + 4\,H_2\,(g) \rightleftharpoons CH_4\,(g) + 2\,H_2S\,(g)$: $[CS_2]$ is doubled.
b. $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$: $[Cl_2]$ is decreased by a factor of 2.
c. $4\,NH_3\,(g) + 5\,O_2\,(g) \rightleftharpoons 4\,NO\,(g) + 6\,H_2O\,(g)$: $[NO]$ is doubled.

Conceptual Answer

1.

a. According to Figure 15.8, we could obtain a graph with the x-axis labeled $[H_2O]\,(l)\,(M)$ and y-axis labeled $[H_2O]\,(g)\,(M)$. The graph should have a positive linear correlation. For any equilibrium concentration of $H_2O\,(g)$, there is only one equilibrium $H_2O\,(l)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]\,(g)$ at equilibrium requires a large $[H_2O]\,(l)$ and vice versa. In this case, the slope of the line is equal to K.

b. According to Figure 15.9, we could obtain a graph with the x-axis labeled $[O2]\,(M)$ and y-axis labeled $[MgO]\,(M)$. Because $O_2\,(g)$ is the only one in gaseous form, the graph would depend on the concentration of O_2.

c. According to Figure 15.8, we could obtain a graph with the x-axis labeled $[O_3]\,(M)$ and y-axis labeled $[O2]\,(M)$. The graph should have a positive linear correlation. For every $3\,O_2\,(g)$ there is $2\,O_3\,(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[O3]\,(g)$ at equilibrium requires a large $[O_2]\,(g)$ and vice versa. In this case, the slope of the line is equal to K.

d. According to figure 15.8, we could obtain a graph with the x-axis labeled $[O2]\,(M)$ and y-axis labeled $[SO2]\,(M)$. The graph should have a positive linear correlation. For every $3\,O_2\,(g)$ there is $2\,SO_2\,(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $O_2\,(g)$ at equilibrium requires a large $SO_2\,(g)$ and vice versa. In this case, the slope of the line is equal to K.

2.

a.

$K = [Na_2CO_3][CO_2][H_2O]$

If $[CO_2]$ is doubled, $[H_2O]$ should be halved if the system is to maintain equilibrium.

b.

$K = \frac{[NF_2]^2}{[N_2F_4]}$

If $[NF_2]$ is decreased by a factor of 2, then $[N_2F_4]$ must also be decreased by a factor of 2 if the system is to maintain equilibrium.

c.

$K = \frac{[HI]^2}{[H_2][I_2]}$

If $[I_2]$ is doubled then $[HI]$ must also be doubled if the system is to maintain equilibrium.

3.

a.

$K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$

If $[CS_2]$ is doubled then $[H_2]$ must be decreased by a factor of $2\sqrt{4} \cong 1.189$ if the system is to maintain equilibrium.

b.

$K = \frac{[PCl_3]}{[Cl_2][PCl_5]}$

If $[Cl_2]$ is halved then $[PCl_5]$ must also be halved if the system is to maintain equilibrium.

c.

$K = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}$

If $[NO]$ is doubled then $[H_2O]$ must also be multiplied by $22/3 \cong 1.587$ if the system is to maintain equilibrium.

Numerical Problems

1. The data in the following table were collected at 450°C for the reaction $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$:

	Equilibrium Partial Pressure (atm)		
P (atm)	NH_3	N_2	H_2
30 (equilibrium)	1.740	6.588	21.58
100	15.20	19.17	65.13
600	321.6	56.74	220.8

The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction $A \rightleftharpoons B + C$, K at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

Experiment	A	B	C
1	2.50 M	2.50 M	2.50 M
2	1.30 atm	1.75 atm	14.15 atm
3	12.61 mol	18.72 mol	6.51 mol

3. The following two reactions are carried out at 823 K:

$$CoO\,(s) + H_2\,(g) \rightleftharpoons Co\,(s) + H_2O\,(g) \text{ with } K = 67 \tag{2.E.12}$$

$$CoO\,(s) + CO\,(g) \rightleftharpoons Co\,(s) + CO_2\,(g) \text{ with } K = 490 \tag{2.E.13}$$

   a. Write the equilibrium expression for each reaction.
   b. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of H_2 or CO plus 0.500 mol CoO.
   c. Using the information provided, calculate Kp for the following reaction:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g) \tag{2.E.14}$$

   d. Describe the shape of the graphs of [reactants] versus [products] as the amount of CoO changes.

4. Hydrogen iodide (HI) is synthesized via $H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$, for which $K_p = 54.5$ at 425°C. Given a 2.0 L vessel containing $1.12 \times 10^{-2}\,mol$ of H_2 and $1.8 \times 10^{-3}\,mol$ of I_2 at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains $3.64 \times 10^{-1}\,mol$ of H_2. Calculate Q and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

Answers

1. The system is not at equilibrium at each of these higher pressures. To reach equilibrium, the reaction will proceed to the right to decrease the pressure because the equilibrium partial pressure is less than the total pressure.

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[15.20]^2}{[19.17][65.13]^3} = 4.4 \times 10^{-5}$$

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[321.6]^2}{[56.74][220.8]^3} = 1.7 \times 10^{-4}$$

2.

1. $K = \frac{[B][C]}{[A]} = \frac{[2.50][2.50]}{[2.50]} = 2.50$
2. $K_p = K(RT)^{\Delta n} \rightarrow K = \frac{K_p}{(RT)^{\Delta n}} = \frac{19.0}{((0.08206\frac{L\cdot atm}{mol\cdot K})(200+273.15)K)^{2-1})} = 0.49$

$$K_p = \frac{(P_B)(P_C)}{(P_A)} = \frac{(1.75)(14.15)}{1.30} = 19.0$$

3. $K = \frac{[B][C]}{[A]^2} = \frac{(18.72)(6.51)}{12.61} = 9.7$

Experiment 1 is about the same as the given K value and thus considered to be about equilibrium. The second experiment has a K value that is about 1 so neither the formation of the reactants or products is favored. The third experiment has a K value that is larger than 1 so the formation of the products is favored.

3.

a.

$K = \frac{[H_2O]}{[H_2]}$

$K = \frac{[CO_2]}{[Co]}$

b.

$[H_2] = [CO] = 0.316\,mol\,H_2 \times \frac{1}{1.00\,L} = 0.316\,M$

$[CoO] = 0.5\,mol\,CoO \times \frac{1}{1.00\,L} = 0.5\,M$

Reaction 1:

$PV = nRT \rightarrow P = \frac{nRT}{V} = (4.65 \times 10^{-3})(0.08206\frac{L\cdot atm}{mol\cdot K})(823\,K) = 0.314$

$[H_2] = 0.316 - x = 0.316 - 0.311 = 4.65x10^{-3}$

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.311)(0.08206\frac{L\cdot atm}{mol\cdot K})(823\,K) = 21.0$

$[H_2O] = x = 0.311$

	H_2	H_2O
I	0.316	0
C	-x	+x
E	0.316-x	x

$K = \frac{[H_2O]}{[H_2]} \rightarrow 67 = \frac{x}{0.316-x} \rightarrow x = 0.311$

Reaction 2:

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.001)(0.08206 \frac{L \cdot atm}{mol \cdot K})(823\ K) = 6.75 \times 10^{-2}\ atm$

$[CO] = 0.316 - x = 0.316 - 0.315 = 0.001\ M$

$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.315)(0.08206 \frac{L \cdot atm}{mol \cdot K})(823\ K) = 21.3\ atm$

$[CO_2] = x = 0.315\ M$

	CO	CO_2
I	0.316	0
C	-x	+x
E	0.316-x	x

$K = \frac{[CO_2]}{[Co]} \rightarrow 490 = \frac{x}{0.316-x} \rightarrow x = 0.315$

c.

$H_2\,(g) + CO_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$

$K_p = \frac{(P_{CO})(P_{H_2O})}{(P_{H_2})(P_{CO_2})} = \frac{(6.75 \times 10^{-2})(21)}{(0.314)(21.3)} = 0.21$

d. The shape of the graphs [reactants] versus [products] does not change as the amount of CoO changes because it is a solid.

4.

$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{n}{V} = \frac{0.101798}{(0.08206 \frac{L \cdot atm}{mol \cdot K})((425+273.15)\ K)} = 1.5 \times 10^{-4}\ M\ HI$

$[HI] = 2x = 2(0.050899) = 0.101798\ atm$

$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} \rightarrow 54.5 = \frac{(2x)^2}{(3.2 \times 10^{-1} - x)(5.16 \times 10^{-2} - x)} \rightarrow x = 0.050899\ atm$

	H_2	I_2	HI
I	3.2×10^{-1}	5.16×10^{-2}	0
C	-x	-x	+2x
E	$3.2 \times 10^{-1} - x$	$5.16 \times 10^{-2} - x$	2x

$PV = nRT \rightarrow P = \frac{nRT}{V} = (5.6 \times 10^{-3})(0.08206 \frac{L \cdot atm}{mol \cdot K})((425 + 273.15)\ K) = 3.2 \times 10^{-1}\ atm$

$[H_2] = 1.12 \times 10^{-2}\ mol\ H_2 \times \frac{1}{2.0\ L} = 5.6 \times 10^{-3}\ M$

$PV = nRT \rightarrow P = \frac{nRT}{V} = (9.0 \times 10^{-4})(0.08206 \frac{L \cdot atm}{mol \cdot K})((425 + 273.15)\ K) = 5.16 \times 10^{-2}\ atm$

$[I_2] = 1.8 \times 10^{-3}\ mol\ I_2 \times \frac{1}{2.0\ L} = 9.0 \times 10^{-4}\ M$

For excess hydrogen:

$Q = \frac{[HI]}{[H_2][I_2]} = \frac{1.8 \times 10^{-3}}{(594.410)(1.09 \times 10^{-3})} = 2.8 \times 10^{-3}$

The reaction will proceed to the right to reach equilibrium.

$$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{0.103162}{(0.08206\frac{L \cdot atm}{mol \cdot K})((425+273.15)\,K)} = 1.8 \times 10^{-3}\,M$$

$$[HI] = 2x = 2(0.051581) = 0.103162\,atm$$

$$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{10.375}{(0.08206\frac{L \cdot atm}{mol \cdot K})((425+273.15)\,K)} = 594.410\,M$$

$$[H_2] = 10.427 - x = 10.427 - 0.051581 = 10.375\,atm$$

$$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{1.9 \times 10^{-5}}{(0.08206\frac{L \cdot atm}{mol \cdot K})((425+273.15)\,K)} = 1.09 \times 10^{-3}\,M$$

$$[I_2] = 5.16 \times 10^{-2} - x = 5.16 \times 10^{-2} - 0.051581 = 1.9 \times 10^{-5}\,atm$$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} \rightarrow 54.5 = \frac{(2x)^2}{(10.427-x)(5.16\times10^{-2}-x)} \rightarrow x = 0.051581\,atm$$

	H_2	I_2	HI
I	10.427	5.16×10^{-2}	0
C	-x	-x	+2x
E	10.427-x	$5.16 \times 10^{-2} - x$	2x

$$PV = nRT \rightarrow P = \frac{nRT}{V} = (0.182\,M)(0.08206\frac{L \cdot atm}{mol \cdot K})((425 + 273.15)\,K) = 10.427\,atm$$

$$[H_2] = 3.64 \times 10^{-1}\,mol\,H_2 \times \frac{1}{2.0\,L} = 0.182\,M$$

15.7: Le Chatelier's Principle

2.E: Chemical Equilibrium (Practice Problems with Answers) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

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3.E: Acid-Base (Practice Questions)

3.E: Acid–Base (more practice questions with answers)

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3.1: A Brief Review and Arrhenius acid-base definition

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. Almost every liquid that we encounter in our daily lives consists of acidic and basic properties, with the exception of water. They have completely different properties and are able to neutralize to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations (Table **3.1.1**).

Table **3.1.1**: General Properties of Acids and Bases

ACIDS	BASES
produce a piercing pain in a wound.	give a slippery feel.
taste sour.	taste bitter.
are colorless when placed in phenolphthalein (an indicator).	are pink when placed in phenolphthalein (an indicator).
are red on blue litmus paper (a pH indicator).	are blue on red litmus paper (a pH indicator).
have a pH<7.	have a pH>7.
produce hydrogen gas when reacted with metals.	
produce carbon dioxide when reacted with carbonates.	
Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are **electrolytes**. Strong acids and bases will be strong electrolytes. Weak acids and bases will be weak electrolytes. This affects the amount of conductivity.

The Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

An Arrhenius acid is a compound that increases the concentration of H^+ ions that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, hydrochloric acid (HCl) dissociates into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment.

Limitation of the Arrhenius Definition of Acids and Bases

The Arrhenius definition can **only** describe acids and bases in an aqueous environment.

In chemistry, acids and bases have been defined differently by three sets of theories: One is the Arrhenius definition defined above, which revolves around the idea that acids are substances that ionize (break off) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions are discussed in detail alter in the chapter and include the Brønsted-Lowry definition the defines acids as substances that donate protons (H^+) whereas bases are substances that accept protons and the Lewis theory of acids and bases states that acids are electron pair acceptors while bases are electron pair donors.

Contributors and Attributions

- Anonymous

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3.2: Brønsted–Lowry Acid-base definition

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Previously, we defined acids and bases as Arrhenius did: An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited. We extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ^1_1H, loses an electron. A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as HSO_4^-, $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{3.2.1}$$

We call the product that remains after an acid donates a proton the **conjugate base** of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{3.2.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{3.2.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{3.2.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{3.2.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{3.2.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{3.2.7}$$

We call the product that results when a base accepts a proton the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{3.2.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{3.2.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{3.2.10}$$

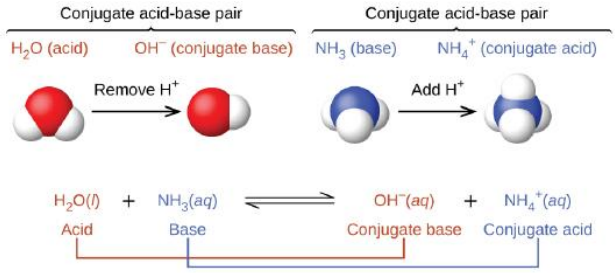
$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{3.2.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{3.2.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{3.2.13}$$

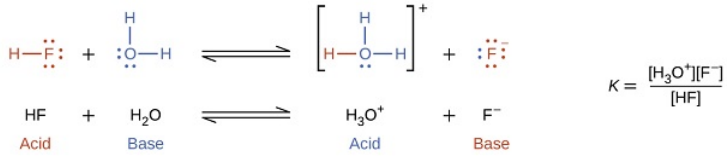
\[\ce{F^- +H^+ \rightleftharpoons HF} \label{16.2.3g} \]

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



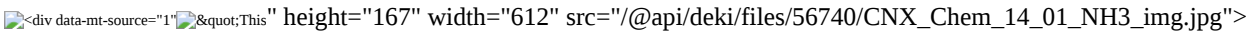
A conjugate acid base pair if when we remove a H plus from the acid to get the conjugate base. Another conjugate acid base pair is when we add H plus to a base to get a conjugate acid. In a reaction: the acid and base are the reactants and the products are the conjugate base and conjugate acid.

The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:

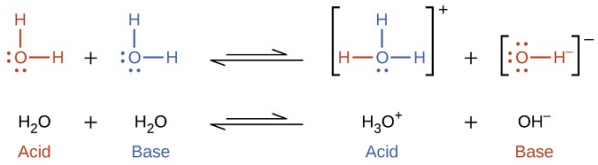


In this reaction HF is treated as the acid and water is treated as the base. The products as H3O plus and F minus. H3O plus is the acid and F minus is the base.

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



Here we have 2 water molecules reacting together. One water molecule is an acid while the second water molecule acts as a base. For the products, we get H3O plus and OH minus. H3O plus is the acid and OH minus is the base.

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HO^-_{(aq)} \quad K_w = [H_3O^+][OH^-]} \tag{3.2.14}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 100-times larger than the value at 25 °C.



A Video Discussing Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs [youtu.be]

Example 3.2.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^{2+} = [OH^-]^{2+} = 1.0 \times 10^{-14}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 3.2.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium determined by the autoionization reaction but it does shift the relative concentrations of $[OH^-]$ and $[H_3O^+]$. Example 16.2.2 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw) [youtu.be]

Example 3.2.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 3.2.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)}} \tag{3.2.15}$$

$$\mathrm{HCO^-_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH^-_{(aq)}} \tag{3.2.16}$$

Example 3.2.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $HSO^-_{3(aq)} + OH^-_{(aq)} \rightleftharpoons SO^{2-}_{3(aq)} + H_2O_{(l)}$
b. $HSO^-_{3(aq)} + HI_{(aq)} \rightleftharpoons H_2SO_{3(aq)} + I^-_{(aq)}$

Example 3.2.4

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer

a. $H_2PO^-_{4(aq)} + HBr_{(aq)} \rightleftharpoons H_3PO_{4(aq)} + Br^-_{(aq)}$
b. $H_2PO^-_{4(aq)} + OH^-_{(aq)} \rightleftharpoons HPO^{2-}_{4(aq)} + H_2O_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, $\mathrm{OH^-}$ when it undergoes autoionization:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$\mathrm{K_w = [H_2O^+][OH^-] = 1.0 \times 10^{-14}\ at\ 25°C}$$

Key Equations

- $$\mathrm{K_w = [H_3O^+][OH^-\ ] = 1.0 \times 10^{-14}\ (at\ 25\ °C)}$$

Glossary

acid ionization

reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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3.3: Autoionization of Water and pH scale

Learning Objectives

- To understand the autoionization reaction of liquid water.
- To know the relationship among pH, pOH, and pK_w.

As you learned previously acids and bases can be defined in several different ways (Table **3.3.1**). Recall that the Arrhenius definition of an acid is a substance that dissociates in water to produce H^+ ions (protons), and an Arrhenius base is a substance that dissociates in water to produce OH^- (hydroxide) ions. According to this view, an acid–base reaction involves the reaction of a proton with a hydroxide ion to form water. Although Brønsted and Lowry defined an acid similarly to Arrhenius by describing an acid as any substance that can donate a proton, the Brønsted–Lowry definition of a base is much more general than the Arrhenius definition. In Brønsted–Lowry terms, a base is any substance that can accept a proton, so a base is not limited to just a hydroxide ion. This means that for every Brønsted–Lowry acid, there exists a corresponding conjugate base with one fewer proton. Consequently, all Brønsted–Lowry acid–base reactions actually involve two conjugate acid–base pairs and the transfer of a proton from one substance (the acid) to another (the base). In contrast, the Lewis definition of acids and bases, focuses on accepting or donating pairs of electrons rather than protons. A Lewis base is an electron-pair donor, and a Lewis acid is an electron-pair acceptor.

Table **3.3.1**: Definitions of Acids and Bases

Definition	Acids	Bases
Arrhenius	H^+ donor	OH^- donor
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Because this chapter deals with acid–base equilibria in aqueous solution, our discussion will use primarily the Brønsted–Lowry definitions and nomenclature. Remember, however, that all three definitions are just different ways of looking at the same kind of reaction: a proton is an acid, and the hydroxide ion is a base—no matter which definition you use. In practice, chemists tend to use whichever definition is most helpful to make a particular point or understand a given system. If, for example, we refer to a base as having one or more lone pairs of electrons that can accept a proton, we are simply combining the Lewis and Brønsted–Lowry definitions to emphasize the characteristic properties of a base.

Acid–Base Properties of Water

Recall that because of its highly polar structure, liquid water can act as either an acid (by donating a proton to a base) or a base (by using a lone pair of electrons to accept a proton). For example, when a strong acid such as HCl dissolves in water, it dissociates into chloride ions (Cl^-) and protons (H^+). The proton, in turn, reacts with a water molecule to form the hydronium ion (H_3O^+):

$$\underset{\text{acid}}{HCl_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightarrow \underset{\text{acid}}{H_3O^+_{(aq)}} + \underset{\text{base}}{Cl^-_{(aq)}} \tag{3.3.1}$$

In this reaction, HCl is the acid, and water acts as a base by accepting an H^+ ion. The reaction in Equation 3.3.1 is often written in a simpler form by removing H_2O from each side:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \tag{3.3.2}$$

In Equation 3.3.2, the hydronium ion is represented by H^+, although free H^+ ions do not exist in liquid water as this reaction demonstrates:

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

Water can also act as an acid, as shown in Equation 3.3.3. In this equilibrium reaction, H_2O donates a proton to NH_3, which acts as a base:

$$\underset{\text{acid}}{H_2O_{(l)}} + \underset{\text{base}}{NH_{3(aq)}} \rightleftharpoons \underset{\text{acid}}{NH^+_{4(aq)}} + \underset{\text{base}}{OH^-_{(aq)}} \tag{3.3.3}$$

Water is thus termed amphiprotic, meaning that it can behave as either an acid or a base, depending on the nature of the other reactant. Notice that Equation 3.3.3 is an equilibrium reaction as indicated by the double arrow and hence has an equilibrium constant associated with it.

The Ion-Product Constant of Liquid Water

Because water is amphiprotic, one water molecule can react with another to form an OH^- ion and an H_3O^+ ion in an autoionization process:

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{3.3.4}$$

The equilibrium constant K for this reaction can be written as follows:

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \approx \frac{[H_3O^+][HO^-]}{(1)^2} = [H_3O^+][HO^-] \tag{3.3.5}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each solute is approximated by the molarity of the solute.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that Ka = $K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation Ka = $K_{eq}(a_{H_2O})$. Because a_{H_2O} = 1 for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and as the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-] \tag{3.3.6}$$

When pure liquid water is in equilibrium with hydronium and hydroxide ions at 25 °C, the concentrations of the hydronium ion and the hydroxide ion are equal:

$$[H_3O^+] = [OH^-] = 1.003 \times 10^{-7}\ M \tag{3.3.7}$$

Thus the number of dissociated water molecules is very small indeed, approximately 2 ppb.

Substituting the values for $[H_3O^+]$ and $[OH^-]$ at 25 °C into this expression

$$K_w = (1.003 \times 10^{-7})(1.003 \times 10^{-7}) = 1.006 \times 10^{-14} \tag{3.3.8}$$

Thus, to three significant figures, $K_w = 1.01 \times 10^{-14}$ *at room temperature*, and

$$K_w = 1.01 \times 10^{-14} = [H_3O^+][OH^-] \tag{3.3.9}$$

.

Like any other equilibrium constant, K_w varies with temperature, ranging from 1.15×10^{-15} at 0 °C to 4.99×10^{-13} at 100 °C.

In pure water, the concentrations of the hydronium ion and the hydroxide ion are equal, and the solution is therefore neutral. If $[H_3O^+] > [OH^-]$, however, the solution is acidic, whereas if $[H_3O^+] < [OH^-]$, the solution is basic. For an aqueous solution, the H_3O^+ concentration is a quantitative measure of acidity: the higher the H_3O^+ concentration, the more acidic the solution. Conversely, the higher the OH^- concentration, the more basic the solution. In most situations that you will encounter, the H_3O^+

and OH^- concentrations from the dissociation of water are so small ($1.003 \times 10^{-7} M$) that they can be ignored in calculating the H_3O^+ or OH^- concentrations of solutions of acids and bases, but this is not always the case.



A Video Describing the Self-Ionization of Water (Kw): Self-Ionization of Water (Kw): [youtu.be]

The Relationship among pH, pOH, and pK_w

The pH scale is a concise way of describing the H_3O^+ concentration and hence the acidity or basicity of a solution. Recall that pH and the H^+ (H_3O^+) concentration are related as follows:

$$pH = -\log_{10}[H^+] \tag{3.3.10}$$

$$[H^+] = 10^{-pH} \tag{3.3.11}$$

Because the scale is logarithmic, a pH difference of 1 between two solutions corresponds to a difference of a factor of 10 in their hydronium ion concentrations. Recall also that the pH of a neutral solution is 7.00 ($[H_3O^+] = 1.0 \times 10^{-7}\ M$), whereas acidic solutions have pH < 7.00 (corresponding to $[H_3O^+] > 1.0 \times 10^{-7}$) and basic solutions have pH > 7.00 (corresponding to $[H_3O^+] < 1.0 \times 10^{-7}$).

Similar notation systems are used to describe many other chemical quantities that contain a large negative exponent. For example, chemists use an analogous pOH scale to describe the hydroxide ion concentration of a solution. The pOH and $[OH^-]$ are related as follows:

$$pOH = -\log_{10}[OH^-] \tag{3.3.12}$$

$$[OH^-] = 10^{-pOH} \tag{3.3.13}$$

The constant K_w can also be expressed using this notation, where $pK_w = -\log\ K_w$.

Because a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$, the pOH of a neutral solution is 7.00. Consequently, the sum of the pH and the pOH for a neutral solution at 25 °C is 7.00 + 7.00 = 14.00. We can show that the sum of pH and pOH is equal to 14.00 for any aqueous solution at 25 °C by taking the negative logarithm of both sides of Equation ???:

$$-\log_{10} K_w = pK_w \tag{3.3.14}$$

$$= -\log([H_3O^+][OH^-]) \tag{3.3.15}$$

$$= (-\log[H_3O^+]) + (-\log[OH^-]) \tag{3.3.16}$$

$$= pH + pOH \tag{3.3.17}$$

Thus at any temperature, $pH + pOH = pK_w$, so at 25 °C, where $K_w = 1.0 \times 10^{-14}$, pH + pOH = 14.00. More generally, the pH of any neutral solution is half of the pK_w at that temperature. The relationship among pH, pOH, and the acidity or basicity of a solution is summarized graphically in Figure **3.3.1** over the common pH range of 0 to 14. Notice the inverse relationship between the pH and pOH scales.

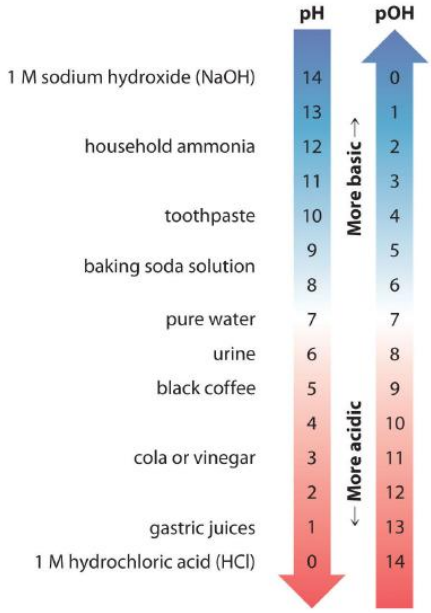


Figure **3.3.1**: The Inverse Relationship between the pH and pOH Scales. As pH decreases, $[H^+]$ and the acidity increase. As pOH increases, $[OH^-]$ and the basicity decrease. Common substances have pH values that range from extremely acidic to extremely basic.

Zero is the most acidic and fourteen is the most basic on the pH scale. Zero is the most basic and fourteen is the most acidic on the pOH scale.

> *For any neutral solution, pH + pOH = 14.00 (at 25 °C) with pH=pOH=7.*



A Video Introduction to pH: Introduction to pH [youtu.be]

Example 3.3.1

The K_w for water at 100 °C is 4.99×10^{-13}. Calculate pK_w for water at this temperature and the pH and the pOH for a neutral aqueous solution at 100 °C. Report pH and pOH values to two decimal places.

Given: K_w

Asked for: pK_w, pH, and pOH

Strategy:

A. Calculate pK_w by taking the negative logarithm of K_w.

B. For a neutral aqueous solution, $[H_3O^+] = [OH^-]$. Use this relationship and Equation 3.3.9 to calculate $[H_3O^+]$ and $[OH^-]$. Then determine the pH and the pOH for the solution.

Solution:

A

Because pK_w is the negative logarithm of Kw, we can write

$$pK_w = -\log K_w = -\log(4.99 \times 10^{-13}) = 12.302$$

The answer is reasonable: K_w is between 10^{-13} and 10^{-12}, so pK_w must be between 12 and 13.

B

Equation ??? shows that $K_w = [H_3O^+][OH^-]$. Because $[H_3O^+] = [OH^-]$ in a neutral solution, we can let $x = [H_3O^+] = [OH^-]$:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (x)(x) = x^2 \\ x &= \sqrt{K_w} \\ &= \sqrt{4.99 \times 10^{-13}} \\ &= 7.06 \times 10^{-7}\ M \end{aligned}$$

Because x is equal to both $[H_3O^+]$ and $[OH^-]$,

$$\begin{aligned} pH = pOH &= -\log(7.06 \times 10^{-7}) \\ &= 6.15 \text{ (to two decimal places)} \end{aligned}$$

We could obtain the same answer more easily (without using logarithms) by using the pK_w. In this case, we know that $pK_w = 12.302$, and from Equation 3.3.17, we know that $pK_w = pH + pOH$. Because $pH = pOH$ in a neutral solution, we can use Equation 3.3.17 directly, setting $pH = pOH = y$. Solving to two decimal places we obtain the following:

$$\begin{aligned} pK_w &= pH + pOH \\ &= y + y \\ &= 2y \\ y &= \frac{pK_w}{2} \\ &= \frac{12.302}{2} \\ &= 6.15 = pH = pOH \end{aligned}$$

? Exercise 3.3.1

Humans maintain an internal temperature of about 37 °C. At this temperature, $K_w = 3.55 \times 10^{-14}$. Calculate pK_w and the pH and the pOH of a neutral solution at 37 °C. Report pH and pOH values to two decimal places.

Answer

- $pK_w = 13.45$
- $pH = pOH = 6.73$

Summary

Water is amphiprotic: it can act as an acid by donating a proton to a base to form the hydroxide ion, or as a base by accepting a proton from an acid to form the hydronium ion (H_3O^+). The autoionization of liquid water produces OH^- and H_3O^+ ions. The equilibrium constant for this reaction is called the ion-product constant of liquid water (Kw) and is defined as $K_w = [H_3O^+][OH^-]$. At 25 °C, K_w is 1.01×10^{-14}; hence $pH + pOH = pK_w = 14.00$.

- For any neutral solution, $pH + pOH = 14.00$ (at 25 °C) and $pH = 1/2pK_w$.
- Ion-product constant of liquid water:

$$K_w = [H_3O^+][OH^-]$$

- Definition of pH:

$$pH = -\log 10[H^+]$$

or

$$[H^+] = 10^{-pH}$$

- Definition of pOH:

$$pOH = -\log_{10}[OH^+]$$

or

$$[OH^-] = 10^{-pOH}$$

- Relationship among pH, pOH, and pK_w:

$$pK_w = pH + pOH$$

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3.4: Acid base ionization constants (Ka and Kb relationship)

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.
- To understand the leveling effect.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{3.4.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \tag{3.4.2}$$

As we noted earlier, because water is the solvent, it has an activity equal to 1, so the $[H_2O]$ term in Equation 3.4.2 is actually the a_{H_2O}, which is equal to 1.

Again, for simplicity, H_3O^+ can be written as H^+ in Equation 3.4.3.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \tag{3.4.3}$$

Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form hydronium ions, H_3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them unitless. The values of K_a for a number of common acids are given in Table 3.4.1.

Table 3.4.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^{9}	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^{2}	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^{1}	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{3.4.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{3.4.5}$$

Once again, the activity of water has a value of 1, so water does not appear in the equilibrium constant expression. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table **3.4.2**.

Table **3.4.2**: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00

*As in Table **3.4.1**.

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{3.4.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{3.4.7}$$

The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{3.4.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{3.4.9}$$

If we add Equations **3.4.6** and **3.4.7**, we obtain the following:

add Equations **3.4.6** and **3.4.7**, we obtain

Reaction	Equilibrium Constants
$\cancel{HCN_{(aq)}} \rightleftharpoons H^+_{(aq)} + \cancel{CN^-_{(aq)}}$	$K_a = [H^+]\,\cancel{[CN^-]} \,/\, \cancel{[HCN]}$
$\cancel{CN^-_{(aq)}} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + \cancel{HCN_{(aq)}}$	$K_b = [OH^-]\,\cancel{[HCN]} \,/\, \cancel{[CN^-]}$
$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$	$K = K_a \times K_b = [H^+][OH^-]$

In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_aK_b = K_w \tag{3.4.10}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{3.4.11}$$

$$K_a = 10^{-pK_a} \tag{3.4.12}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{3.4.13}$$

$$K_b = 10^{-pK_b} \tag{3.4.14}$$

Similarly, Equation 3.4.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{3.4.15}$$

At 25 °C, this becomes

$$pK_a + pK_b = 14.00 \tag{3.4.16}$$

The values of pK_a and pK_b are given for several common acids and bases in Tables 3.4.1 and 3.4.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a million times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

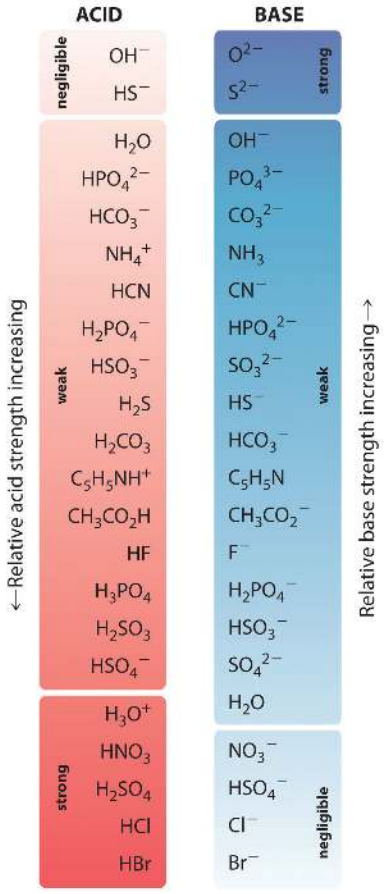


Figure 3.4.1: The Relative Strengths of Some Common Conjugate Acid–Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Strong acids are H3O plus, HNO3, H2SO4, HCl, and HBr. Negligible acids are HS minus and OH minus. Stron bases are O negative 2, S negative 2. Negligible bases are NO3 minus, HSO4 minus, Cl minus, and Br minus.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 3.4.1. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This

order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure **3.4.2** are the common strong acids; at the top right are the most common strong bases. Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

> *The conjugate base of a strong acid is a weak base and vice versa.*

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\textbf{stronger acid} + \textbf{stronger base} \rightleftharpoons \textbf{weaker acid} + \textbf{weaker base}$$

In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{3.4.17}$$

In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$\mathrm{CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CH_3CO_{2(aq)}{}^-}$$

Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

> *All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.*

Example 3.4.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation **3.4.10**. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equations **3.4.15** and **3.4.16**. Use the relationships pK = −log K and $K = 10^{-pK}$ (Equations **3.4.11** and **3.4.13**) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation **3.4.16**: $pK_a + pK_b = pK_w = 14.00$. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 3.4.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27$$

$$pKa + pK_b = 14.00$$

$$pK_a = 10.73$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

? Exercise 3.4.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

- $K_a = 1.4 \times 10^{-4}$ for lactic acid;
- pK_b = 10.14 and
- $K_b = 7.2 \times 10^{-11}$ for the lactate ion



A Video Calculating pH in Strong Acid or Strong Base Solutions: Calculating pH in Strong Acid or Strong Base Solutions [youtu.be]

Solutions of Strong Acids and Bases: The Leveling Effect

You will notice in Table 3.4.1 that acids like H_2SO_4 and HNO_3 lie above the hydronium ion, meaning that they have pK_a values less than zero and are stronger acids than the H_3O^+ ion. Recall from Chapter 4 that the acidic proton in virtually all oxoacids is bonded to one of the oxygen atoms of the oxoanion. Thus nitric acid should properly be written as $HONO_2$. Unfortunately, however, the formulas of oxoacids are almost always written with hydrogen on the left and oxygen on the right, giving HNO_3 instead. In fact, all six of the common strong acids that we first encountered in Chapter 4 have pK_a values less than zero, which means that they have a

greater tendency to lose a proton than does the H_3O^+ ion. Conversely, the conjugate bases of these strong acids are weaker bases than water. Consequently, the proton-transfer equilibria for these strong acids lie far to the right, and adding any of the common strong acids to water results in an essentially stoichiometric reaction of the acid with water to form a solution of the H_3O^+ ion and the conjugate base of the acid.

Although K_a for HI is about 108 greater than K_a for HNO_3, the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I− or NO_3^-. In fact, a 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water. Consequently, it is impossible to distinguish between the strengths of acids such as HI and HNO3 in aqueous solution, and an alternative approach must be used to determine their relative acid strengths.

One method is to use a solvent such as anhydrous acetic acid. Because acetic acid is a stronger acid than water, it must also be a weaker base, with a lesser tendency to accept a proton than H_2O. Measurements of the conductivity of 0.1 M solutions of both HI and HNO_3 in acetic acid show that HI is completely dissociated, but HNO_3 is only partially dissociated and behaves like a weak acid in this solvent. This result clearly tells us that HI is a stronger acid than HNO_3. The relative order of acid strengths and approximate K_a and pK_a values for the strong acids at the top of Table 3.4.1 were determined using measurements like this and different nonaqueous solvents.

> *In aqueous solutions, H_3O^+ is the strongest acid and OH^- is the strongest base that can exist in equilibrium with H_2O.*

The leveling effect applies to solutions of strong bases as well: In aqueous solution, any base stronger than OH− is leveled to the strength of OH− because OH− is the strongest base that can exist in equilibrium with water. Salts such as K_2O, $NaOCH_3$ (sodium methoxide), and $NaNH_2$ (sodamide, or sodium amide), whose anions are the conjugate bases of species that would lie below water in Table 3.4.2, are all strong bases that react essentially completely (and often violently) with water, accepting a proton to give a solution of OH^- and the corresponding cation:

$$K_2O_{(s)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + 2K^+_{(aq)} \tag{3.4.18}$$

$$NaOCH_{3(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + CH_3OH_{(aq)} \tag{3.4.19}$$

$$NaNH_{2(s)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)} + NH_{3(aq)} \tag{3.4.20}$$

Other examples that you may encounter are potassium hydride (KH) and organometallic compounds such as methyl lithium (CH_3Li).

Polyprotic Acids and Bases

As you learned, polyprotic acids such as H_2SO_4, H_3PO_4, and H_2CO_3 contain more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases. Consider H_2SO_4, for example:

$$HSO^-_{4(aq)} \rightleftharpoons SO^{2-}_{4(aq)} + H^+_{(aq)} \quad pK_a = -2$$

The equilibrium in the first reaction lies far to the right, consistent with H_2SO_4 being a strong acid. In contrast, in the second reaction, appreciable quantities of both HSO_4^- and SO_4^{2-} are present at equilibrium.

> *For a polyprotic acid, acid strength decreases and the pK_a increases with the sequential loss of each proton.*

The hydrogen sulfate ion (HSO_4^-) is both the conjugate base of H_2SO_4 and the conjugate acid of SO_4^{2-}. Just like water, HSO4− can therefore act as either an acid or a base, depending on whether the other reactant is a stronger acid or a stronger base. Conversely, the sulfate ion (SO_4^{2-}) is a polyprotic base that is capable of accepting two protons in a stepwise manner:

$$SO_{4(aq)}^{2-} + H_2O_{(aq)} \rightleftharpoons HSO_{4(aq)}^{-} + OH_{(aq)}^{-}$$

$$HSO_{4(aq)}^{-} + H_2O_{(aq)} \rightleftharpoons H_2SO_{4(aq)} + OH_{(aq)}^{-} \tag{3.4.21}$$

Like any other conjugate acid–base pair, the strengths of the conjugate acids and bases are related by $pK_a + pK_b$ = pKw. Consider, for example, the HSO_4^-/SO_4^{2-} conjugate acid–base pair. From Table **3.4.1**, we see that the pK_a of HSO_4^- is 1.99. Hence the pK_b of SO_4^{2-} is 14.00 − 1.99 = 12.01. Thus sulfate is a rather weak base, whereas OH^- is a strong base, so the equilibrium shown in Equation **3.4.21** lies to the left. The HSO_4^- ion is also a very weak base (pK_a of H_2SO_4 = 2.0, pK_b of $HSO_4^- = 14 - (-2.0) = 16$), which is consistent with what we expect for the conjugate base of a strong acid.

Example 3.4.2

Predict whether the equilibrium for each reaction lies to the left or the right as written.

- $NH_{4(aq)}^{+} + PO_{4(aq)}^{3-} \rightleftharpoons NH_{3(aq)} + HPO_{4(aq)}^{2-}$
- $CH_3CH_2CO_2H_{(aq)} + CN_{(aq)}^{-} \rightleftharpoons CH_3CH_2CO_{2(aq)}^{-} + HCN_{(aq)}$

Given: balanced chemical equation

Asked for: equilibrium position

Strategy:

Identify the conjugate acid–base pairs in each reaction. Then refer to Tables **3.4.1**and**3.4.2** and Figure **3.4.2** to determine which is the stronger acid and base. Equilibrium **always** favors the formation of the weaker acid–base pair.

Solution:

The conjugate acid–base pairs are NH_4^+/NH_3 and HPO_4^{2-}/PO_4^{3-}. According to Tables **3.4.1** and **3.4.2**, NH_4^+ is a stronger acid ($pK_a = 9.25$) than HPO_4^{2-} (pKa = 12.32), and PO_4^{3-} is a stronger base ($pK_b = 1.68$) than NH_3 ($pK_b = 4.75$). The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{NH_{4(aq)}^{+}} + \underset{\text{stronger base}}{PO_{4(aq)}^{3-}} \rightleftharpoons \underset{\text{weaker base}}{NH_{3(aq)}} + \underset{\text{weaker acid}}{HPO_{4(aq)}^{2-}}$$

The conjugate acid–base pairs are $CH_3CH_2CO_2H/CH_3CH_2CO_2^-$ and HCN/CN^-. According to Table **3.4.1**, HCN is a weak acid (pKa = 9.21) and CN^- is a moderately weak base (pKb = 4.79). Propionic acid ($CH_3CH_2CO_2H$) is not listed in Table **3.4.1**, however. In a situation like this, the best approach is to look for a similar compound whose acid–base properties are listed. For example, propionic acid and acetic acid are identical except for the groups attached to the carbon atom of the carboxylic acid ($-CH_2CH_3$ versus $-CH_3$), so we might expect the two compounds to have similar acid–base properties. In particular, we would expect the pK_a of propionic acid to be similar in magnitude to the pK_a of acetic acid. (In fact, the pK_a of propionic acid is 4.87, compared to 4.76 for acetic acid, which makes propionic acid a slightly weaker acid than acetic acid.) Thus propionic acid should be a significantly stronger acid than HCN. Because the stronger acid forms the weaker conjugate base, we predict that cyanide will be a stronger base than propionate. The equilibrium will therefore lie to the right, favoring the formation of the weaker acid–base pair:

$$\underset{\text{stronger acid}}{CH_3CH_2CO_2H_{(aq)}} + \underset{\text{stronger base}}{CN_{(aq)}^{-}} \rightleftharpoons \underset{\text{weaker base}}{CH_3CH_2CO_{2(aq)}^{-}} + \underset{\text{weaker acid}}{HCN_{(aq)}}$$

Exercise 3.4.1

Predict whether the equilibrium for each reaction lies to the left or the right as written.

a. $H_2O_{(l)} + HS_{(aq)}^{-} \rightleftharpoons OH_{(aq)}^{-} + H_2S_{(aq)}$
b. $HCO_{2(aq)}^{-} + HSO_{4(aq)}^{-} \rightleftharpoons HCO_2H_{(aq)} + SO_{4(aq)}^{2-}$

Answer a

left

Answer b

left



A Video Discussing Polyprotic Acids: Polyprotic Acids [youtu.be]

Summary

Acid–base reactions always contain two conjugate acid–base pairs. Each acid and each base has an associated ionization constant that corresponds to its acid or base strength. Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (K_a). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (K_b). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair. No acid stronger than H_3O^+ and no base stronger than OH^- can exist in aqueous solution, leading to the phenomenon known as the leveling effect. Polyprotic acids (and bases) lose (and gain) protons in a stepwise manner, with the fully protonated species being the strongest acid and the fully deprotonated species the strongest base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$

$$K_a = 10^{-pK_a}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$

$$K_b = 10^{-pK_b}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w$$

$$pK_a + pK_b = 14.00 \text{ at } 25°C$$

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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SECTION OVERVIEW

3.5: 3.5 Percentage ionization (% ionization)

3.5.1: Weak Acids

3.5.2: Weak Bases

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3.5.1: Weak Acids

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure 3.5.1.1 lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure 3.5.1.1: 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:

$$\%\ \text{ionization} = \frac{[H3O+]_{eq}}{[HA]_0} \times 100\% \tag{3.5.1.1}$$

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 3.5.1.1: 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 3.5.1.1) 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 3.5.1.1

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 3.5.1.1 lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, **B**:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_b = \frac{[HB+][OH-]}{[B]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3CO_2^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2H}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_b = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\mathrm{HA - A^-}$:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

with $K_a = \frac{[H3O+][A-]}{[HA]}$.

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq)$$

with $K_b = \frac{[HA][OH]}{[A-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$
$$2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_a \times K_b = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion ($\mathrm{CH_3COO^-}$), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_a \times K_b = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_w$$

The extent to which an acid, **HA**, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, **HA**, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure **3.5.1.2**).

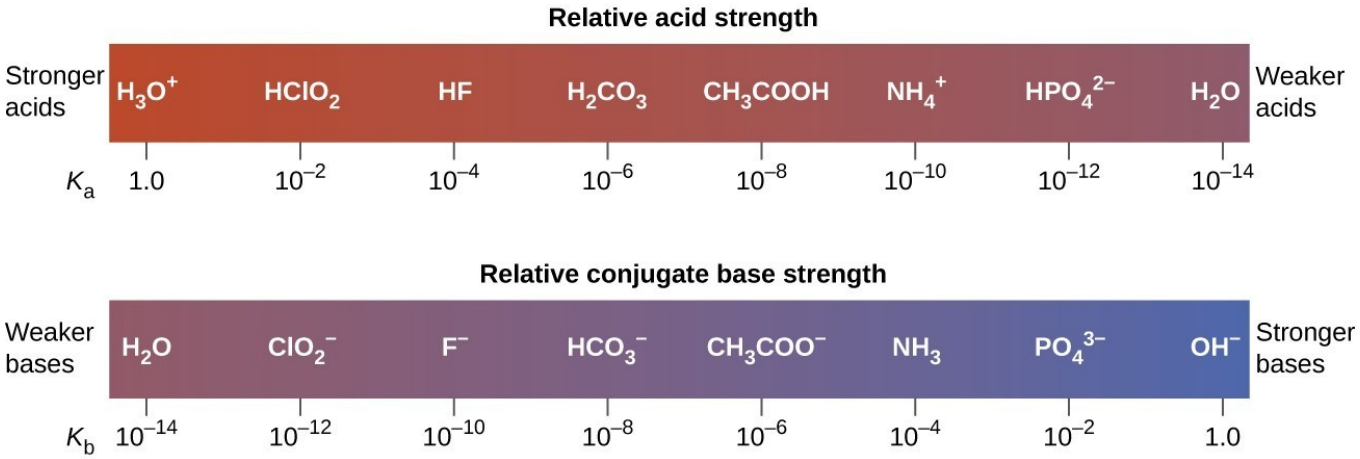


Figure **3.5.1.2**: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure **3.5.1.3** 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 **3.5.1.3** 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 **3.5.1.3** 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 **3.5.1.3** 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.

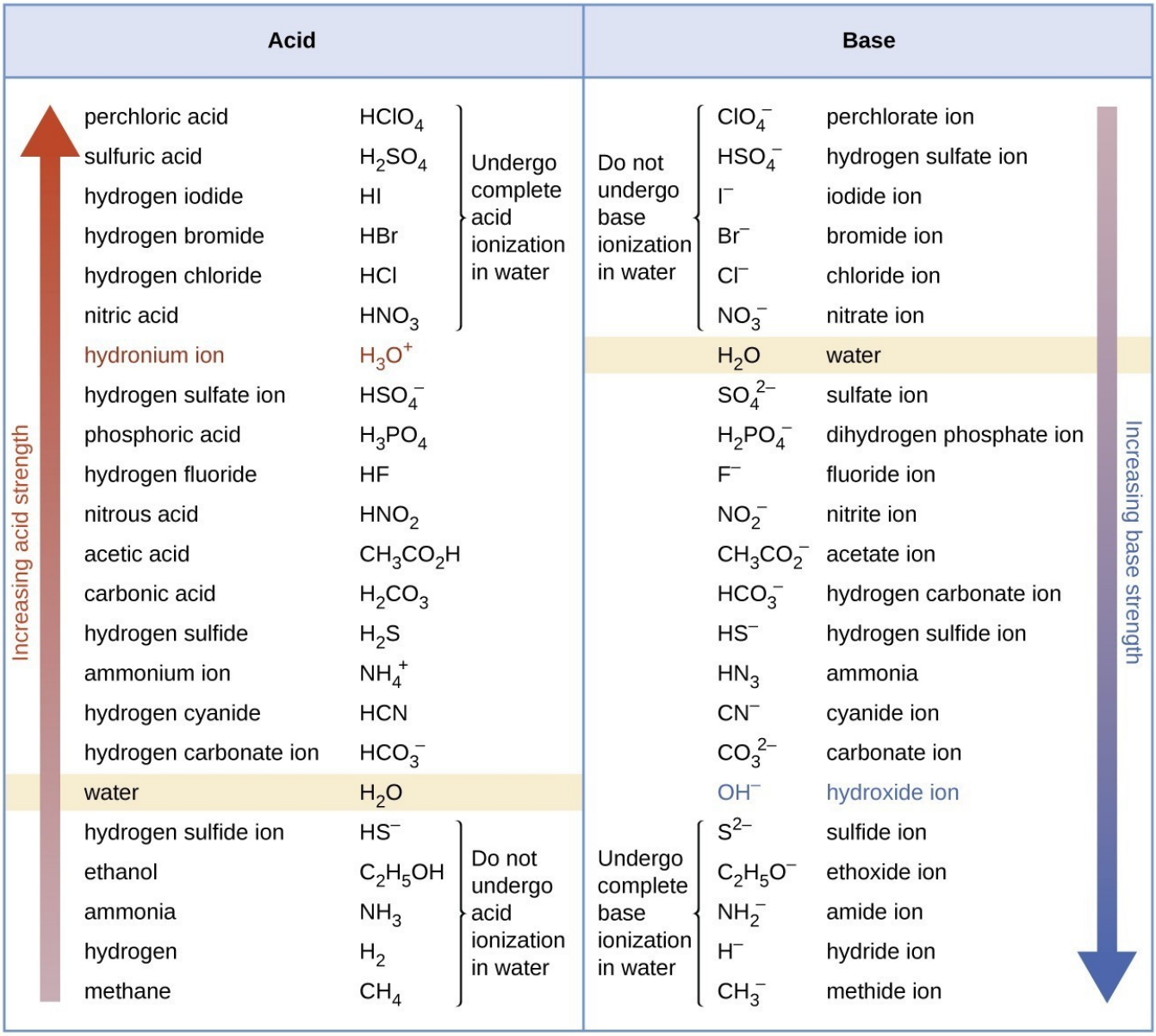


Figure **3.5.1.3**: The chart shows the relative strengths of conjugate acid-base pairs.

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 **3.5.1.3**. 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 **3.5.1.2**: 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 3.5.1.2

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 3.5.1.4). 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 **3.5.1.4**: 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 **3.5.1.1**: 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 **3.5.1.1** 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 3.5.1.5: 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 3.5.1.2 and Table E2.

Table 3.5.1.2: 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 3.5.1.3: 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:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H3O+][CH3CO2-]}{[CH3CO2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

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Exercise 3.5.1.3

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 3.5.1.4: 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 3.5.1.4

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 3.5.1.5: Determination of K_a or K_b from pH

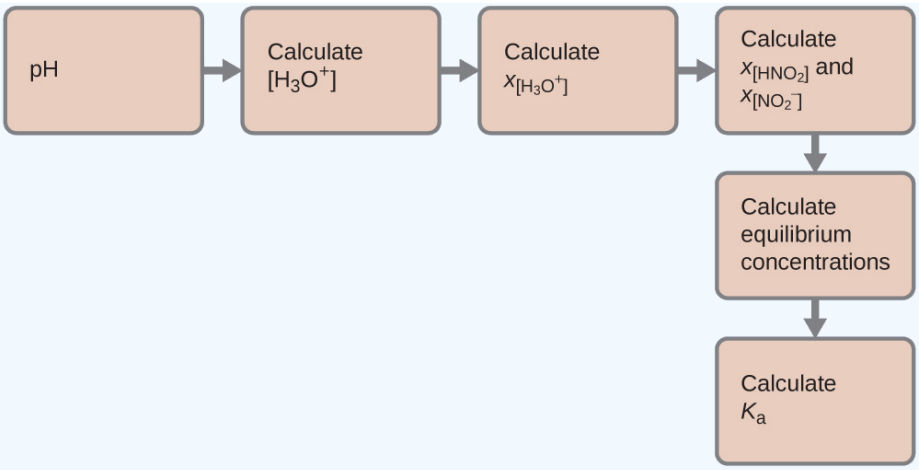
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

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 3.5.1.5

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 3.5.1.6: 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:

$$[\mathrm{H_3O^+}] = \; 0 + x = 0 + 9.8 \times 10^{-3} \; M.$$
$$= 9.8 \times 10^{-3} \; M$$

The pH of the solution can be found by taking the negative log of the $[\mathrm{H_3O^+}]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

? Exercise 3.5.1.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[\mathrm{CH_3CO_2^-}]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\frac{[CH3CO2-]}{[CH3CO2H]_{initial}} \times 100$.

Answer

percent ionization = 1.3%

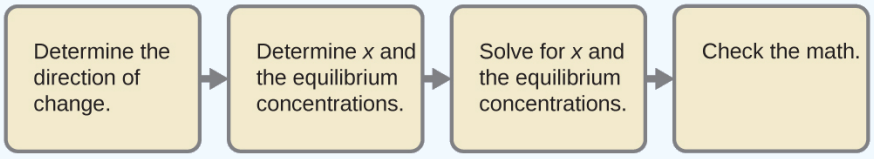
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

✓ Example 3.5.1.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(\mathrm{CH_3})_3\mathrm{N}(aq) + \mathrm{H_2O}(l) \rightleftharpoons (\mathrm{CH_3})_3\mathrm{NH^+}(aq) + \mathrm{OH^-}(aq) \quad K_b = 6.3 \times 10^{-5}$$

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 3.5.1.6. 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 3.5.1.7

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.

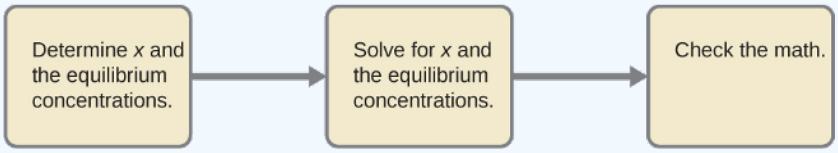
Example 3.5.1.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O $\rightleftharpoons$	H_3O^+	+ SO_4^{2-}
Initial concentration (*M*)	0.50	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.50 + (-x) = 0.50 - x$	$0 + x = x$	$0 + x = x$

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H3O+][SO4^{2-}]}{[HSO4-]} = \frac{(x)(x)}{0.50 - x}$$

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 3.5.1.8

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 $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 3.5.1.6).

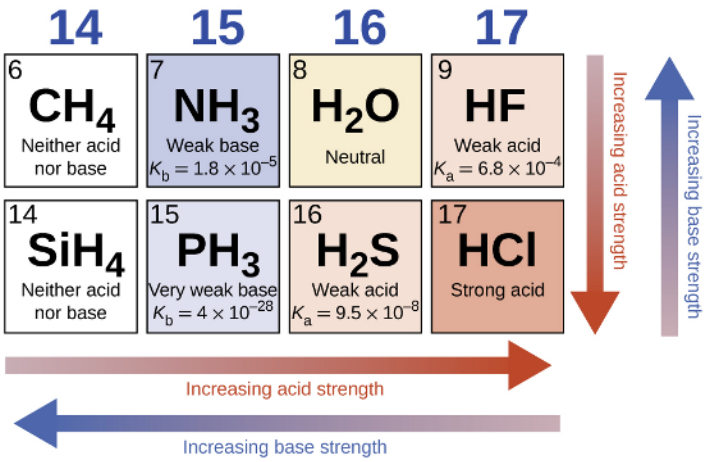
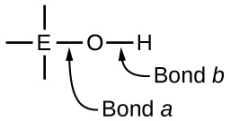


Figure 3.5.1.6: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

This diagram has two rows and four columns. Red arrows point left across the bottom of the figure and down at the right side and are labeled “Increasing acid strength.” Blue arrows point left across the bottom and up at the right side of the figure and are labeled “Increasing base strength.” The first column is labeled 14 at the top and two white squares are beneath it. The first has the number 6 in the upper left corner and the formula C H subscript 4 in the center along with designation Neither acid nor base. The second square contains the number 14 in the upper left corner, the formula C H subscript 4 at the center and the designation Neither acid nor base. The second column is labeled 15 at the top and two blue squares are beneath it. The first has the number 7 in the upper left corner and the formula N H subscript 3 in the center along with the designation Weak base and K subscript b equals 1.8 times 10 superscript negative 5. The second square contains the number 15 in the upper left corner, the formula P H subscript 3 at the center and the designation Very weak base and K subscript b equals 4 times 10 superscript negative 28. The third column is labeled 16 at the top and two squares are beneath it. The first is shaded tan and has the number 8 in the upper left corner and the formula H subscript 2 O in the center along with the designation neutral. The second square is shaded pink, contains the number 16 in the upper left corner, the formula H subscript 2 S at the center and the designation Weak acid and K subscript a equals 9.5 times 10 superscript negative 8. The fourth column is labeled 17 at the top and two squares are beneath it. The first is shaded pink, has the number 9 in the upper left corner and the formula H F in the center along with the designation Weak acid and K subscript a equals 6.8 times 10 superscript negative 4. The second square is shaded a deeper pink, contains the number 17 in the upper left corner, the formula H C l at the center, and the designation Strong acid.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



A diagram is shown that includes a central atom designated with the letter E. Single bonds extend above, below, left, and right of the E. An O atom is bonded to the right of the E, and an arrow points to the bond labeling it, “Bond a.” An H atom is single bonded to the right of the O atom. An arrow pointing to this bond connects it to the label, “Bond b.”

If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure **3.5.1.7**).

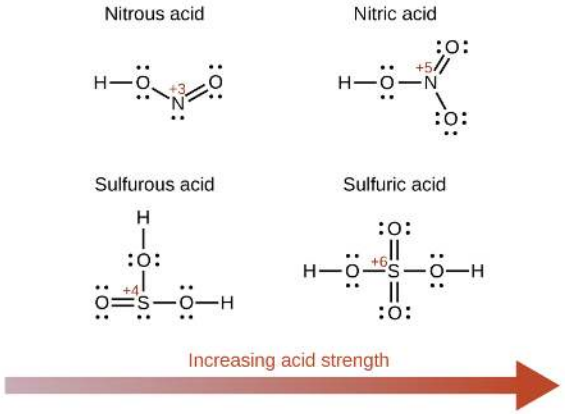


Figure **3.5.1.7**: As the oxidation number of the central atom E increases, the acidity also increases.

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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3.5.2: Weak Bases

The pH of a solution of a weak base can be calculated in a way which is very similar to that used for a weak acid. Instead of an acid constant K_a, a base constant K_b must be used. If a weak base B accepts protons from water according to the equation

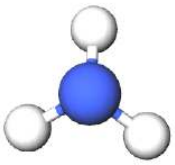
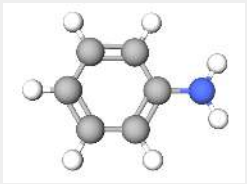
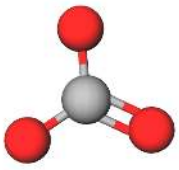
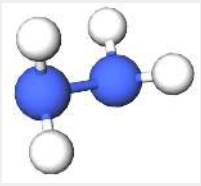
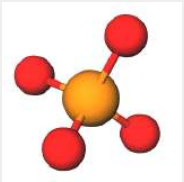
$$\mathrm{B} + \mathrm{H_2O} \rightleftharpoons \mathrm{BH^+} + \mathrm{OH^-} \tag{3.5.2.1}$$

then the base constant is defined by the expression

$$K_b = \frac{\mathrm{BH^+}\ \mathrm{OH^-}}{\mathrm{B}} \tag{3.5.2.2}$$

A list of K_b values for selected bases arranged in order of strength is given in the table below. This table is part of our larger collection of acid-base resources.

Table **3.5.2.1**: The Base Constants for Some Bases at 25°C. Taken from Hogfelt, E. Perrin, D. D. Stability Constants of Metal Ion Complexes, 1st ed. Oxford; New Pergamon, 1979-1982. International Union of Pure and Applied Chemistry, Commission on Equilibrium. ISBN: 0080209580

Base	Formula and Ionization Equation	K_b	Molecular Shape
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.77×10^{-5}	
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	3.9×10^{-10}	
Carbonate ion	$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$	2.1×10^{-4}	
Hydrazine	$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$	$K_1 = 1.2 \times 10^{-6}$ $K_2 = 1.3 \times 10^{-15}$	
Hydride ion	$H^- + H_2O \rightarrow H_2 + OH^-$	1.0	
Phosphate ion	$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$	5.9×10^{-3}	
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.6×10^{-9}	

To find the pH we follow the same general procedure as in the case of a weak acid. If the stoichiometric concentration of the base is indicated by c_b, the result is entirely analogous to equation 4 in the section on the pH of weak acids; namely,

$$K_b = \frac{[\mathrm{OH^-}]^2}{c_b - [\mathrm{OH^-}]} \tag{3.5.2.3}$$

Under most circumstances we can make the approximation

$$c_b - [OH^-] \approx c_b$$

in which case Equation 3.5.2.3 reduces to the approximation

$$[OH^-] \approx \sqrt{K_b c_b} \tag{3.5.2.4}$$

which is identical to the expression obtained in the acid case (approximation shown in equation 6 in the section on the pH of weak acids) except that OH^- replaces H_3O^+ and *b* replaces *a*. Once we have found the hydroxide-ion concentration from this approximation, we can then easily find the pOH, and from it the pH.

Example 3.5.2.1: pH using K_b

Using the value for K_b listed in the table, find the pH of 0.100 *M* NH_3.

Solution

It is not a bad idea to guess an approximate pH before embarking on the calculation. Since we have a dilute solution of a weak base, we expect the solution to be only mildly basic. A pH of 13 or 14 would be too basic, while a pH of 8 or 9 is too close to neutral. A pH of 10 or 11 seems reasonable. Using Equation 3.5.2.4 we have

$$\begin{aligned}[\text{OH}^-] &= \sqrt{K_b c_b} \\ &= \sqrt{1.8 \times 10^{-5}\ \text{mol L}^{-1} \times 0.100\ \text{mol L}^{-1}} \\ &= \sqrt{1.8 \times 10^{-6}\ \text{mol}^2\ \text{L}^{-2}} \\ &= 1.34 \times 10^{-3}\ \text{mol L}^{-1}\end{aligned}$$

Checking the accuracy of the approximation, we find

$$\frac{[\text{OH}^-]}{c_b} = \frac{1.34 \times 10^{-3}}{0.1} \approx 1\ \text{percent}$$

The approximation is valid, and we thus proceed to find the pOH.

$$\text{pOH} = -\log\frac{[\text{OH}^-]}{\text{mol L}^{-1}} = -\log(1.34 \times 10^{-3}) = 2.87$$

From which

$$pH = 14.00 - pOH = 14.00 - 2.87 = 11.13$$

This calculated value checks well with our initial guess.

Occasionally we will find that the approximation

$$c_b - [OH^-] \approx c_b$$

is not valid, in which case we must use a series of successive approximations similar to that outlined above for acids. The appropriate formula can be derived from Equation 3.5.2.3 and reads

$$[OH^-] \approx \sqrt{K_b(c_b - [OH^-])}$$

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3.6: The Acid-Base Properties of Ions and Salts

Learning Objectives

- To recognize salts that will produce acidic, basic, or neutral solutions in water
- To understand the Lewis acidity of small, highly-charged metal ions in water

A neutralization reaction can be defined as the reaction of an acid and a base to produce a salt and water. That is, another cation, such as Na^+, replaces the proton on the acid. An example is the reaction of CH_3CO_2H, a weak acid, with $NaOH$, a strong base:

$$\underset{\text{acid}}{CH_3CO_2H_{(l)}} + \underset{\text{base}}{NaOH_{(s)}} \xrightarrow{H_2O} \underset{\text{salt}}{H_2OCH_3CO_2Na_{(aq)}} + \underset{\text{water}}{H_2O_{(l)}}$$

Depending on the acid–base properties of its component ions, however, a salt can dissolve in water to produce a neutral solution, a basic solution, or an acidic solution.

When a salt such as $NaCl$ dissolves in water, it produces $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ ions. Using a Lewis approach, the Na^+ ion can be viewed as an acid because it is an electron pair acceptor, although its low charge and relatively large radius make it a very weak acid. The Cl^- ion is the conjugate base of the strong acid HCl, so it has essentially no basic character. Consequently, dissolving $NaCl$ in water has no effect on the pH of a solution, and the solution remains neutral.

Now let's compare this behavior to the behavior of aqueous solutions of potassium cyanide and sodium acetate. Again, the cations (K^+ and Na^+) have essentially no acidic character, but the anions (CN^- and $CH_3CO_2^-$) are weak bases that can react with water because they are the conjugate bases of the weak acids HCN and acetic acid, respectively.

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

$$CH_3CO^2_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3CO_2H_{(aq)} + OH^-_{(aq)}$$

Neither reaction proceeds very far to the right as written because the formation of the weaker acid–base pair is favored. Both HCN and acetic acid are stronger acids than water, and hydroxide is a stronger base than either acetate or cyanide, so in both cases, the equilibrium lies to the left. Nonetheless, each of these reactions generates enough hydroxide ions to produce a basic solution. For example, the pH of a 0.1 M solution of sodium acetate or potassium cyanide at 25°C is 8.8 or 11.1, respectively. From Table **3.6.1** and Figure **3.6.1**, we can see that CN^- is a stronger base ($pK_b = 4.79$) than acetate ($pK_b = 9.24$), which is consistent with KCN producing a more basic solution than sodium acetate at the same concentration.

In contrast, the conjugate acid of a weak base should be a weak acid (Equation 3.6.1). For example, ammonium chloride and pyridinium chloride are salts produced by reacting ammonia and pyridine, respectively, with HCl. As you already know, the chloride ion is such a weak base that it does not react with water. In contrast, the cations of the two salts are weak acids that react with water as follows:

$$NH^+_{4(aq)} + H_2O_{(l)} \rightleftharpoons HH_{3(aq)} + H_3O^+_{(aq)} \tag{3.6.1}$$

$$C_5H_5NH^+_{(aq)} + H_2O_{(l)} \rightleftharpoons C_5H_5NH_{(aq)} + H_3O^+_{(aq)} \tag{3.6.2}$$

Equation 3.6.1 indicates that H_3O^+ is a stronger acid than either NH_4^+ or $C_5H_5NH^+$, and conversely, ammonia and pyridine are both stronger bases than water. The equilibrium will therefore lie far to the left in both cases, favoring the weaker acid–base pair. The H_3O^+ concentration produced by the reactions is great enough, however, to decrease the pH of the solution significantly: the pH of a 0.10 M solution of ammonium chloride or pyridinium chloride at 25°C is 5.13 or 3.12, respectively. This is consistent with the information shown in Figure 16.2, indicating that the pyridinium ion is more acidic than the ammonium ion.

What happens with aqueous solutions of a salt such as ammonium acetate, where both the cation and the anion can react separately with water to produce an acid and a base, respectively? According to Figure 16.10, the ammonium ion will lower the pH, while according to Equation 3.6.2, the acetate ion will raise the pH. This particular case is unusual, in that the cation is as strong an acid as the anion is a base (pKa ≈ pKb). Consequently, the two effects cancel, and the solution remains neutral. With salts in which the

cation is a stronger acid than the anion is a base, the final solution has a $pH < 7.00$. Conversely, if the cation is a weaker acid than the anion is a base, the final solution has a $pH > 7.00$.

Solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion (part (a) in Figure **3.6.1**). A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

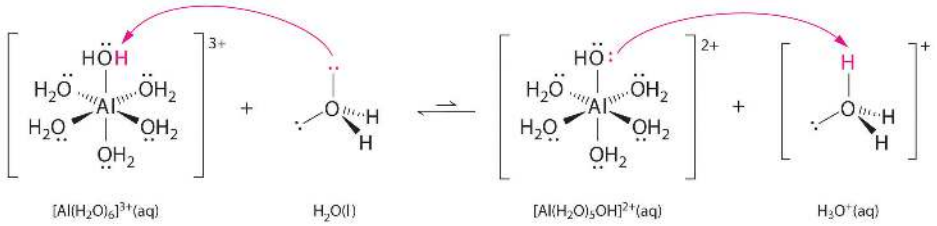


Figure **3.6.1**. With less electron density between the O atoms and the H atoms, the **O–H** bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion.

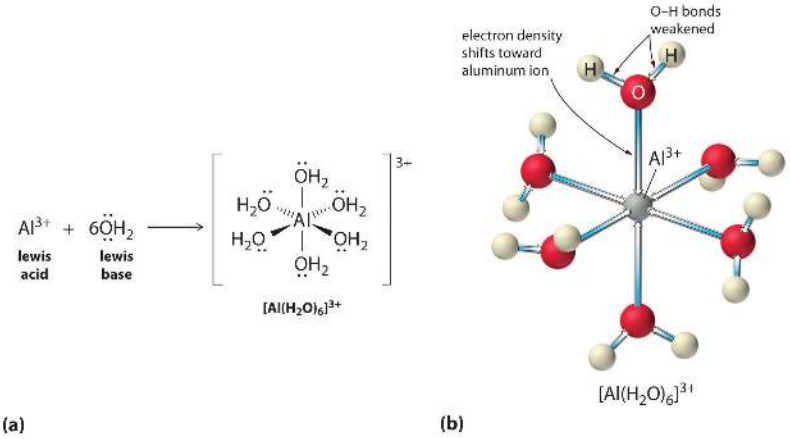


Figure **3.6.1**: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton.

On the left is the reaction of Al three plus with six OH2 which produces [AL(H2O)6] three plus. On the right is the molecular structure of [Al(H2O)6] three plus.

The magnitude of this effect depends on the following two factors (Figure **3.6.2**):

1. The charge on the metal ion. A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.
2. The radius of the metal ion. For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

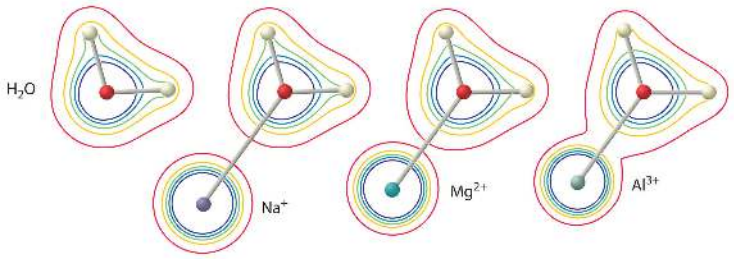


Figure **3.6.2**: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases.

Thus aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \tag{3.6.3}$$

The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameter for predicting the effect of a metal ion on the acidity of coordinated water molecules is the charge-to-radius ratio of the metal ion. A number of pairs of metal ions that lie on a diagonal line in the periodic table, such as Li^+ and Mg^{2+} or Ca^{2+} and Y^{3+}, have different sizes and charges, but similar charge-to-radius ratios. As a result, these pairs of metal ions have similar effects on the acidity of coordinated water molecules, and they often exhibit other significant similarities in chemistry as well.

> *Solutions of small, highly charged metal ions in water are acidic.*

Reactions such as those discussed in this section, in which a salt reacts with water to give an acidic or basic solution, are often called hydrolysis reactions. Using a separate name for this type of reaction is unfortunate because it suggests that they are somehow different. In fact, hydrolysis reactions are just acid–base reactions in which the acid is a cation or the base is an anion; they obey the same principles and rules as all other acid–base reactions.

> *A hydrolysis reaction is an acid–base reaction.*

Example 3.6.1

Predict whether aqueous solutions of these compounds are acidic, basic, or neutral.

a. KNO_3
b. $CrBr_3 cdot H_2O$
c. Na_2SO_4

Given: compound

Asked for: acidity or basicity of aqueous solution

Strategy:

A. Assess the acid–base properties of the cation and the anion. If the cation is a weak Lewis acid, it will not affect the pH of the solution. If the cation is the conjugate acid of a weak base or a relatively highly charged metal cation, however, it will react with water to produce an acidic solution.
B. f the anion is the conjugate base of a strong acid, it will not affect the pH of the solution. If, however, the anion is the conjugate base of a weak acid, the solution will be basic.

Solution:

a

A. The K^+ cation has a small positive charge (+1) and a relatively large radius (because it is in the fourth row of the periodic table), so it is a very weak Lewis acid.

B. The NO_3- anion is the conjugate base of a strong acid, so it has essentially no basic character (Table 16.1). Hence neither the cation nor the anion will react with water to produce H^+ or OH^-, and the solution will be neutral.

b.

A. The Cr^{3+} ion is a relatively highly charged metal cation that should behave similarly to the Al^{3+} ion and form the $[Cr(H2O)_6]^{3+}$ complex, which will behave as a weak acid:

$$Cr(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons Cr(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)}$$

B. The Br^- anion is a very weak base (it is the conjugate base of the strong acid HBr), so it does not affect the pH of the solution. Hence the solution will be acidic.

c.

A. The Na^+ ion, like the K^+, is a very weak acid, so it should not affect the acidity of the solution.
B. In contrast, SO_4^{2-} is the conjugate base of HSO_4^-, which is a weak acid. Hence the SO_4^{2-} ion will react with water as shown in Figure 16.6 to give a slightly basic solution.

? Exercise 3.6.1

Predict whether aqueous solutions of the following are acidic, basic, or neutral.

a. KI
b. $Mg(ClO_4)_2$
c. $NaHS$

Answer a

neutral

Answer b

acidic

Answer c

basic (due to the reaction of $\mathbf{HS^-}$ with water to form $\mathbf{H_2S}$ and $\mathbf{OH^-}$)

Summary

A salt can dissolve in water to produce a neutral, a basic, or an acidic solution, depending on whether it contains the conjugate base of a weak acid as the anion (A^-), the conjugate acid of a weak base as the cation (BH^+), or both. Salts that contain small, highly charged metal ions produce acidic solutions in water. The reaction of a salt with water to produce an acidic or a basic solution is called a hydrolysis reaction.

Key Takeaways

- Acid–base reactions always contain two conjugate acid–base pairs.
- Each acid and each base has an associated ionization constant that corresponds to its acid or base strength.

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3.7: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an electron-pair transfer reaction, clearly identifying the donor and acceptor.
- Give an example of a *Lewis acid-base reaction* that does not involve protons.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

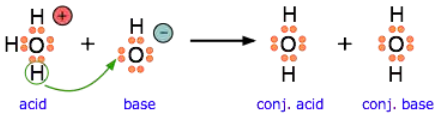
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

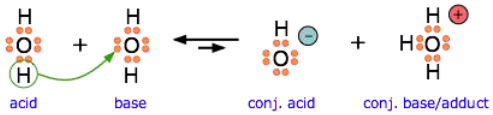
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



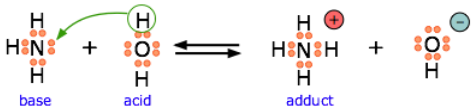
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

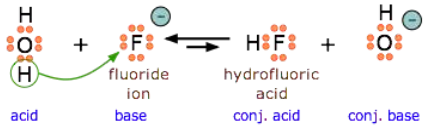
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.



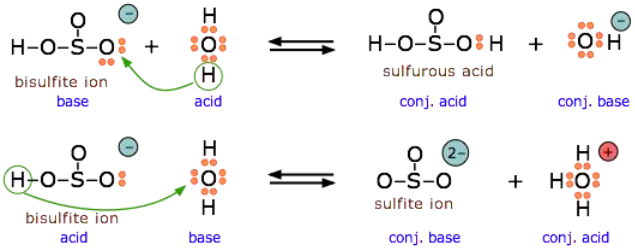
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.



Because **HF** is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.



The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$\mathbf{BF_3 + NH_3 \rightarrow F_3B{-}NH_3} \tag{3.7.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

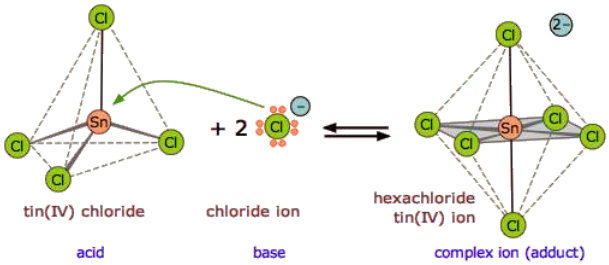


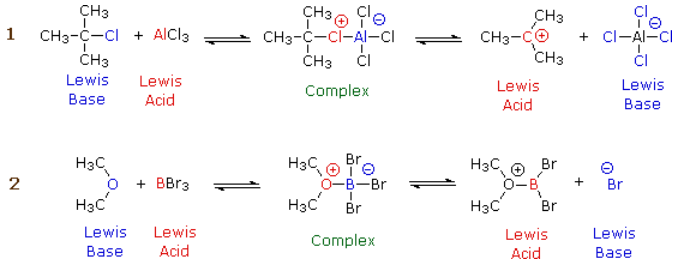
Figure **3.7.1**: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

? Exercise 3.7.1

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2\,CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table **3.7.1**). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table **3.7.1** indicates:

Table **3.7.1**: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\,CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\,C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\,HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\,HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\,H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

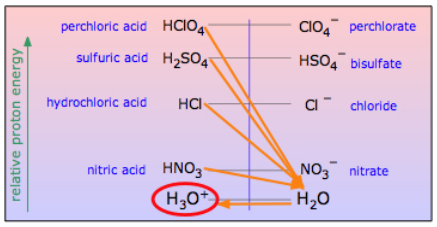


Figure **3.7.2**: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

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3.8: Acid-Base Chemistry in day today life (heartburn and Kitchen Chemistry))

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 **3.8.1**). 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.

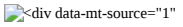


Figure **3.8.1**: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

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 3.8.1: 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?

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$$

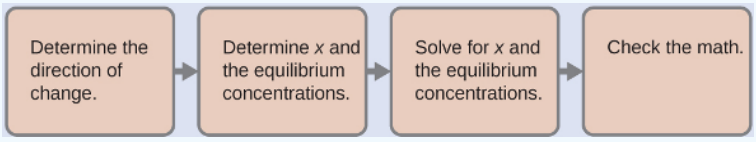
Solution

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 3.8.1

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 3.8.2: 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 3.8.2

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 3.8.3: 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 3.8.3

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 **3.8.2**) 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.

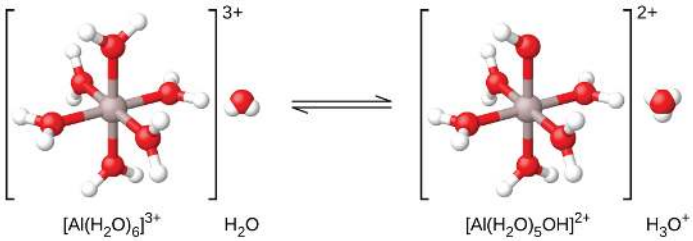


Figure **3.8.2**: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

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:

$$Fe(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Fe(H_2O)_5(OH)^{2+}(aq) \quad K_a = 2.74$$

$$Cu(H_2O)_6{}^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cu(H_2O)_5(OH)^{+}(aq) \quad K_a = 6.3$$

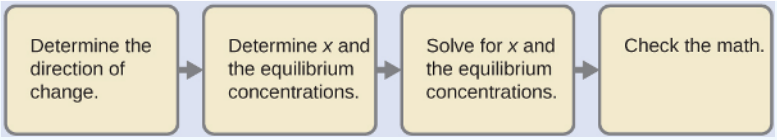
$$Zn(H_2O)_4{}^{2+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^{+}(aq) \quad K_a = 9.6$$

✔ Example 3.8.4: 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 3.8.4

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.E: Acid-Base (Practice Questions)

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), $\mathbf{NO_3^-}$ **(CB)**; CN^-(BB), H_2O(BA), HCN(CA), $\mathbf{OH^-}$ (CB); H_2SO_4(BA), Cl^-(BB), HCl(CA), $\mathbf{HSO_4^-}$ **(CB)**; $\mathbf{HSO_4^-}$ **(BA)**, OH^-(BB), $\mathbf{SO_4^{2-}}$ **(CB)**, H_2O(CA); O^{2-}(BB), H2O(BA) $\mathbf{OH^-}$ (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), $\mathbf{NH_2^-}$ **(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. $\mathbf{H_2PO_4^-}$
c. S^{2-}
d. $\mathbf{CO_3^{2-}}$
e. $\mathbf{HSO_4^-}$

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. $\mathbf{HPO_4^-}$
c. Br^-
d. $\mathbf{NH_4^+}$
e. $\mathbf{ASO_4^{3-}}$

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

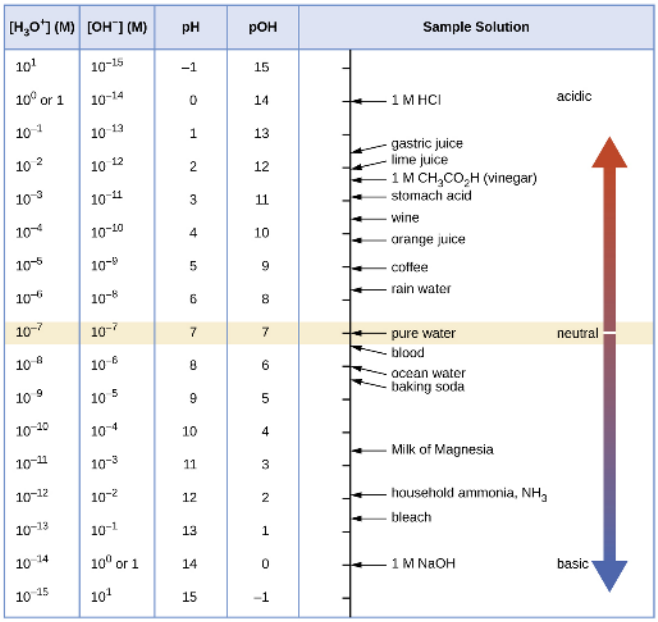
What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

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. $\mathbf{K_b = 1.8 \times 10^{-5}}$;
b. $\mathbf{K_a = 4.5 \times 10^{-4}}$;
c. $\mathbf{K_b = 7.4 \times 10^{-5}}$;
d. $\mathbf{K_a = 5.6 \times 10^{-10}}$

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

$\mathbf{K_a = 1.2 \times 10^{-2}}$

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. $\mathbf{K_b = 4.3 \times 10^{-12}}$;
b. $\mathbf{K_a = 1.4 \times 10^{-10}}$;
c. $\mathbf{K_b = 1 \times 10^{-7}}$;
d. $\mathbf{K_b = 4.2 \times 10^{-3}}$;
e. $\mathbf{K_b = 4.2 \times 10^{-3}}$;
f. $\mathbf{K_b = 8.3 \times 10^{-13}}$

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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3.E: Acid–Base (more practice questions with answers)

16.1: Acids and Bases: A Brief Review

16.2: Brønsted–Lowry Acids and Bases

Conceptual Problems

1. Identify the conjugate acid–base pairs in each equilibrium.
   a. $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
   b. $C_3H_7NO_2(aq) + H_3O^+(aq) \rightleftharpoons C_3H_8NO_2^+(aq) + H_2O(l)$
   c. $CH_3O_2H(aq) + NH_3(aq) \rightleftharpoons CH_3CO_2^-(aq) + NH_4^+(aq)$
   d. $SbF_5(aq) + 2\,HF(aq) \rightleftharpoons H_2F^+(aq) + SbF_6^-(aq)$
2. Identify the conjugate acid–base pairs in each equilibrium.
   a. $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
   b. $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$
   c. $C_3H_7NO_2(aq) + OH^-(aq) \rightleftharpoons C_3H_6NO_2^-(aq) + H_2O(l)$
   d. $CH_3CO_2H(aq) + 2\,HF(aq) \rightleftharpoons CH_3C(OH)_2^+(aq) + HF_2^-(aq)$
3. Salts such as NaH contain the hydride ion (H^-). When sodium hydride is added to water, it produces hydrogen gas in a highly vigorous reaction. Write a balanced chemical equation for this reaction and identify the conjugate acid–base pairs.
4. Write the expression for K_a for each reaction.
   a. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
   b. $formic\ acid(aq) + H_2O(l) \rightleftharpoons formate(aq) + H_3O^+(aq)$
   c. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
5. Write an expression for the ionization constant K_b for each reaction.
   a. $OCH_3^-(aq) + H_2O(l) \rightleftharpoons HOCH_3(aq) + OH^-(aq)$
   b. $NH_2^-(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + OH^-(aq)$
   c. $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$
6. Predict whether each equilibrium lies primarily to the left or to the right.
   a. $HBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Br^-(aq)$
   b. $NaH(s) + NH_3(aq) \rightleftharpoons H_2(g) + NaNH_2(s)$
   c. $OCH_3^-(aq) + NH_3(aq) \rightleftharpoons CH_3OH(aq) + NH_2^-(aq)$
   d. $NH_3(aq) + HCl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$
7. Species that are strong bases in water, such as CH_3^-, NH_2^-, and S^{2-}, are leveled to the strength of OH^-, the conjugate base of H_2O. Because their relative base strengths are indistinguishable in water, suggest a method for identifying which is the strongest base. How would you distinguish between the strength of the acids HIO_3, H_2SO_4, and $HClO_4$?
8. Is it accurate to say that a 2.0 M solution of H_2SO_4, which contains two acidic protons per molecule, is 4.0 M in H^+? Explain your answer.
9. The alkalinity of soil is defined by the following equation: alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$. The source of both HCO_3^- and CO_3^{2-} is H_2CO_3. Explain why the basicity of soil is defined in this way.
10. Why are aqueous solutions of salts such as $CaCl_2$ neutral? Why is an aqueous solution of $NaNH_2$ basic?
11. Predict whether the aqueous solutions of the following are acidic, basic, or neutral.
    a. Li_3N
    b. NaH
    c. KBr
    d. $C_2H_5NH_3Cl$
12. When each compound is added to water, would you expect the pH of the solution to increase, decrease, or remain the same?
    a. $LiCH_3$
    b. $MgCl_2$

c. K_2O

d. $(CH_3)_2NH_2^+Br^-$

13. Which complex ion would you expect to be more acidic: $Pb(H_2O)_4^{2+}$ or $Sn(H_2O)_4^{2+}$? Why?

14. Would you expect $Sn(H_2O)_4^{2+}$ or $Sn(H_2O)_6^{4+}$ to be more acidic in aqueous solutions? Why?

15. Is it possible to arrange the hydrides LiH, RbH, KH, CsH, and NaH in order of increasing base strength in aqueous solution? Why or why not?

Conceptual Answer

1.

a. $\underset{\text{acid}}{HSO_4^-}(aq) + \underset{\text{base}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate base}}{SO_4^{2-}}(aq) + \underset{\text{conjugate acid}}{H_3O^+}(aq)$

b. $\underset{\text{base}}{C_3H_7NO_2}(aq) + \underset{\text{acid}}{H_3O^+}(aq) \rightleftharpoons \underset{\text{conjugate acid}}{C_3H_8NO_2^+}(aq) + \underset{\text{conjugate base}}{H_2O}(l)$

c. $\underset{\text{acid}}{HOAc}(aq) + \underset{\text{base}}{NH_3}(aq) \rightleftharpoons \underset{\text{conjugate base}}{CH_3CO_2^-}(aq) + \underset{\text{conjugate acid}}{NH_4^+}(aq)$

d. $\underset{\text{acid}}{SbF_5}(aq) + 2\,\underset{\text{base}}{HF}(aq) \rightleftharpoons \underset{\text{conjugate acid}}{H_2F^+}(aq) + \underset{\text{conjugate base}}{SbF_6^-}(aq)$

2.

a. $\underset{\text{acid}}{HF}(aq) + \underset{\text{base}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+}(aq) + \underset{\text{conjugate base}}{F^-}(aq)$

b. $\underset{\text{base}}{CH_3CH_2NH_2}(aq) + \underset{\text{acid}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate acid}}{CH_3CH_2NH_3^+}(aq) + \underset{\text{conjugate base}}{OH^-}(aq)$

c. $\underset{\text{acid}}{C_3H_7NO_2}(aq) + \underset{\text{base}}{OH^-}(aq) \rightleftharpoons \underset{\text{conjugate base}}{C_3H_6NO_2^-}(aq) + \underset{\text{conjugate acid}}{H_2O}(l)$

d. $\underset{\text{base}}{CH_3CO_2H}(aq) + 2\,\underset{\text{acid}}{HF}(aq) \rightleftharpoons \underset{\text{conjugate acid}}{CH_3C(OH)_2^+}(aq) + \underset{\text{conjugate base}}{HF_2^-}(aq)$

3. $\underset{\text{base}}{NaH}(s) + \underset{\text{acid}}{H_2O}(l) \rightleftharpoons \underset{\text{conjugate acid}}{H_2}(g) + \underset{\text{conjugate base}}{NaOH}(aq)$

4.

a. $K_a = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

b. $K_a = \frac{[formate][H_3O^+]}{[formic\ acid]}$

c. $K_a = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$

5.

a. $K_b = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

b. $K_b = \frac{[NH_3][OH^-]}{[NH_2^-]}$

c. $K_b = \frac{[HS^-][OH^-]}{[S^{2-}]}$

6. Strong acids have the smaller pK_a.

a. Equilibrium lies primarily to the right because HBr ($pK_a = -8.7$) is a stronger acid than H_3O^+ ($pK_a = -1.7$) and H_2O ($pK_a = 14$) is a stronger base than Br^- ($pK_a = -8.7$).

b. Equilibrium lies primarily to the left because H_2 ($pK_a = 36$) is a stronger acid than NH_3 ($pK_a = 38$) and ($NaNH_2$) ($pK_a = 38$) is a stronger base than NaH ($pK_a = 35$).

c. Equilibrium lies primarily to the left because CH_3OH ($pK_a = 17$) is a stronger acid than NH_3 ($pK_a = 38$) and NH_2^- ($pK_a = 38$) is a stronger base than OCH_3^- ($pK_a = 25$).

d. Equilibrium lies to the right because HCl ($pK_a = -7$) is a stronger acid than NH_4^+ ($pK_a = 9.3$) and NH_3 is a stronger base than Cl^- ($pK_a = -7$).

7. To identify the strongest base we can determine their weakest conjugate acid. The conjugate acids of CH_3^-, NH_2^-, and S_2^- are CH_4, NH_3, and HS^-, respectively. Next, we consider that acidity increases with positive charge on the molecule, thus ruling out that S_2^- is the weakest base. Finally, we consider that acidity increases with electronegativity, therefore NH_3 is the second most basic and CH_4 is the most basic. To distinguish between the strength of the acids HIO_3, H_2SO_4, and $HClO_4$ we can consider that the higher electronegativity and oxidation state of the central nonmetal is the more acidic, therefore the order of acidity is: $HIO_3 < H_2SO_4 < HClO_4$ because electronegativity and oxidation state increases as follows: $I(+5) < S(+6) < Cl(+7)$.

8. It is not accurate to say that a 2.0 M solution of H_2SO_4, which contains two acidic protons per molecule, is 4.0 M in H^+ because a 2.0 M solution of H_2SO_4 is equivalent to 4.0 N in H^+.

$$\frac{2.0\,mol\,H_2SO_4}{1\,L} \times \frac{2\,eq\,H^+}{1\,mol\,H_2SO_4} = \frac{4\,eq\,H^+}{L} = 4\,N\,H^+$$

9. Alkalinity is a measure of acid neutralizing capability. The basicity of the soil is defined this way because bases such as HCO_3^- and CO_3^{2-} can neutralize acids in soil. Because most soil has a pH between 6 and 8, alkalinity can be estimated by its carbonate species alone. At a near neutral pH, most carbonate species are bicarbonate.

10. Aqueous solutions of salts such as $CaCl_2$ are neutral because it is created from hydrochloric acid (a strong acid) and calcium hydroxide (a strong base). An aqueous solution of $NaNH_2$ is basic because it can deprotonate alkynes, alcohols, and a host of other functional groups with acidic protons such as esters and ketones.

11.

a. Li_3N is a base because the lone pair on the nitrogen can accept a proton.

b. NaH is a base because the hydrogen has a negative charge.

c. KBr is neutral because it is formed from HBr (a strong acid) and KOH (a strong base).

d. $C_2H_5NH_3Cl$ is acidic because it can donate a proton.

12.

a. The pH is expected to increase. $\underset{\text{acid}}{LiCH_3\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate base}}{LiOH\,(aq)} + \underset{\text{conjugate acid}}{CH_4\,(aq)}$

b. The pH is expected to increase. $\underset{\text{acid}}{MgCl_2\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate acid}}{2\,HCl\,(aq)} + \underset{\text{conjugate base}}{MgO\,(aq)}$

c. The pH is expected to remain the same. $K_2O\,(aq) + H_2O\,(l) \rightleftharpoons 2\,KOH\,(aq)$

d. The pH is expected to increase. $\underset{\text{acid}}{(CH_3)_2NH_2^+Br^-\,(aq)} + \underset{\text{base}}{H_2O\,(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+\,(aq)} + \underset{\text{conjugate base}}{(CH_3)_2NH\,(aq)}$

13. $Sn(H_2O)_4^{2+}$ is expected to be more acidic than $Pb(H_2O)_4^{2+}$ because Sn is more electronegative than Pb.

14. $Sn(H_2O)_6^{4+}$ is expected to be more acidic than $Sn(H_2O)_4^{2+}$ because the charge on Sn is greater ($4^+ > 2^+$).

15. Yes, it is possible the order of increasing base strength is: $LiH < NaH < RbH < CsH$ because increasing base strength is dependent on decreasing electronegativity.

Numerical Problems

1. Arrange these acids in order of increasing strength.
   - acid A: $pK_a = 1.52$
   - acid B: $pK_a = 6.93$
   - acid C: $pK_a = 3.86$

   Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?

2. Arrange these bases in order of increasing strength:
   - base A: $pK_b = 13.10$
   - base B: $pK_b = 8.74$
   - base C: $pK_b = 11.87$

   Given solutions with the same initial concentration of each base, which would have the highest percent ionization?

3. Calculate the K_a and the pK_a of the conjugate acid of a base with each pK_b value.
   a. 3.80
   b. 7.90
   c. 13.70
   d. 1.40
   e. −2.50
4. Benzoic acid is a food preservative with a pK_a of 4.20. Determine the K_b and the pK_b for the benzoate ion.
5. Determine K_a and pK_a of boric acid $[B(OH)_3]$, solutions of which are occasionally used as an eyewash; the pK_b of its conjugate base is 4.80.

Numerical Answers

1. Acids in order of increasing strength: $acid\ B < acid\ C < acid\ A$. Given the same initial concentration of each acid, the highest percent of ionization is acid A because it is the strongest acid.

2. Bases in order of increasing strength: $base\ A < base\ C < base\ B$. Given the solutions with the same initial concentration of each base, the higher percent of ionization is base A because it is the weakest base.

3.

a.

$$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 3.80 = 10.2$$

$$K_a = 10^{-pK_a} = 10^{-10.2} = 6.31 \times 10^{-11}$$

b.

$$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 6.10$$

$$K_a = 10^{-pK_a} = 10^{-6.10} = 7.94 \times 10^{-7}$$

c.

$$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 3.000 \times 10^{-1}$$

$$K_a = 10^{-pK_a} = 10^{-3.000 \times 10^{-1}} = -5.012 \times 10^{-1}$$

d.

$$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 1.40 = 12.6$$

$$K_a = 10^{-pK_a} = 10^{-12.6} = 2.51 \times 10^{-13}$$

e. $pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 7.90 = 16.5$

$$K_a = 10^{-pK_a} = 10^{-16.5} = 3.16 \times 10^{-17}$$

4.

$$pK_a + pK_b = 14 \rightarrow pK_b = 14 - pK_a = 14 - 4.20 = 9.80$$

$$K_b = 10^{-pK_b} = 10^{-9.80} = 1.58 \times 10^{-10}$$

5.

$$pK_a + pK_b = 14 \rightarrow pK_a = 14 - pK_b = 14 - 4.80 = 9.20$$

$$K_a = 10^{-pK_a} = 10^{-9.20} = 6.31 \times 10^{-10}$$

16.3: The Autoionization of Water

Conceptual Problems

1. What is the relationship between the value of the equilibrium constant for the autoionization of liquid water and the tabulated value of the ion-product constant of liquid water (K_w)?

2. The density of liquid water decreases as the temperature increases from 25°C to 50°C. Will this effect cause K_w to increase or decrease? Why?
3. Show that water is amphiprotic by writing balanced chemical equations for the reactions of water with HNO_3 and NH_3. In which reaction does water act as the acid? In which does it act as the base?
4. Write a chemical equation for each of the following.
   a. Nitric acid is added to water.
   b. Potassium hydroxide is added to water.
   c. Calcium hydroxide is added to water.
   d. Sulfuric acid is added to water.
5. Show that K for the sum of the following reactions is equal to K_w.

$$HMnO_4\,(aq) \rightleftharpoons H^+\,(aq) + MnO_4^-\,(aq) \tag{3.E.1}$$

$$MnO_4^-\,(aq) + H_2O\,(l) \rightarrow HMnO_4\,(aq) + OH^-\,(aq) \tag{3.E.2}$$

Conceptual Answers

1.

$$K_{auto} = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \tag{3.E.3}$$

$$K_w = [H_3O^+][OH^-] = K_{auto}[H_2O]^2 \tag{3.E.4}$$

2. This will affect K_w as it is dependent on temperature. As the temperature increases, an endothermic process occurs (energy must be absorbed to break the bonds). Consequently, according to Le Chatelier, an increase in temperature favors the forward reaction thus the position of equilibrium shifts toward the right-hand side and K_w becomes larger.

3.
Water acts as the base:

$$H_2O\,(l) + HNO_3\,(g) \rightarrow H_3O^+\,(aq) + NO_3^-\,(aq) \tag{3.E.5}$$

Water acts as the acid:

$$H_2O\,(l) + NH_3\,(g) \rightarrow OH^-\,(aq) + NH_4^-\,(aq) \tag{3.E.6}$$

4.

a. $HNO_3\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HNO_2^-\,(aq)$

b. $KOH\,(s) + H_2O\,(l) \rightleftharpoons K^-\,(aq) + OH^-\,(aq)$

c. $Ca(OH)_2\,(s) + H_2O\,(l) \rightleftharpoons Ca^{2+}\,(aq) + 2\,OH^-\,(aq)$

d. $H_2SO_4\,(aq) + H_2O\,(l) \rightleftharpoons HSO_4^-\,(aq) + H^+\,(aq)$

5.

$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$

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

Numerical Problems

1. The autoionization of sulfuric acid can be described by the following chemical equation:

$$H_2SO_4\,(l) + H_2SO_4\,(aq) \rightleftharpoons H_3SO_4^+\,(aq) + HSO_4^-\,(aq) \tag{3.E.7}$$

   At 25°C, $K = 3 \times 10^{-4}$. Write an equilibrium constant expression for $K_{H_2SO_4}$ that is analogous to K_w. The density of H_2SO_4 is $1.8\frac{g}{cm^3}$ at 25°C. What is the concentration of $H_3SO_4^+$? What fraction of H_2SO_4 is ionized?
2. An aqueous solution of a substance is found to have $[H_3O]^+ = 2.48 \times 10^{-8}\ M$. Is the solution acidic, neutral, or basic?
3. The pH of a solution is 5.63. What is its pOH? What is the $[OH^-]$? Is the solution acidic or basic?

4. State whether each solution is acidic, neutral, or basic.
    a. $[H_3O^+] = 8.6 \times 10^{-3}\ M$
    b. $[H_3O^+] = 3.7 \times 10^{-9}\ M$
    c. $[H_3O^+] = 2.1 \times 10^{-7}\ M$
    d. $[H_3O^+] = 1.4 \times 10^{-6}\ M$
5. Calculate the pH and the pOH of each solution.
    a. 0.15 $M\ HBr$
    b. 0.03 $M\ KOH$
    c. $2.3 \times 10^{-3}\ M\ HNO_3$
    d. $9.78 \times 10^{-2}\ M\ NaOH$
    e. 0.00017 $M\ HCl$
    f. 5.78 $M\ HI$
6. Calculate the pH and the pOH of each solution.
    a. 25.0 mL of $2.3 \times 10^{-2}\ M\ HCl$, diluted to 100 mL
    b. 5.0 mL of $1.87\ M\ NaOH$, diluted to 125 mL
    c. 5.0 mL of $5.98\ M\ HCl$ added to 100 mL of water
    d. 25.0 mL of $3.7\ M\ HNO_3$ added to 250 mL of water
    e. 35.0 mL of $0.046\ M\ HI$ added to 500 mL of water
    f. 15.0 mL of $0.0087\ M\ KOH$ added to 250 mL of water.
7. The pH of stomach acid is approximately 1.5. What is the $[H^+]$?
8. Given the pH values in parentheses, what is the $[H^+]$ of each solution?
    a. household bleach (11.4)
    b. milk (6.5)
    c. orange juice (3.5)
    d. seawater (8.5)
    e. tomato juice (4.2)
9. A reaction requires the addition of 250.0 mL of a solution with a pH of 3.50. What mass of HCl (in milligrams) must be dissolved in 250 mL of water to produce a solution with this pH?
10. If you require 333 mL of a pH 12.50 solution, how would you prepare it using a 0.500 M sodium hydroxide stock solution?

Numerical Answers

1.

$$K_{H_2SO_4} = [H_3SO_4^+][HSO_4^-] = K[H_2SO_4]_2 \tag{3.E.8}$$

$$[H_3SO_4^+] = 0.3\,M \tag{3.E.9}$$

So the fraction ionized is 0.02.

2. The solution is basic because the $pH = -log([H_3O^+]) = -log(2.48 \times 10^{-8}) = 7.61 > 7$.

3.

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 5.63 = 8.37$

$[OH^-] = 10^{-pOH} = -4.27 \times 10^{-9}$

The $pH = 5.63 < 7$, therefore the solution is acidic.

4.

a. The solution is acidic. $pH = -log([H_3O^+]) = -log(8.6 \times 10^{-3}) = 2.1 < 7$

b. The solution is basic. $pH = -log([H_3O^+]) = -log(3.7 \times 10^{-9}) = 8.4 > 7$

c. The solution is acidic. $pH = -log([H_3O^+]) = -log(2.1 \times 10^{-7}) = 6.7 < 7$

d. The solution is acidic. $pH = -log([H_3O^+]) = -log(1.4 \times 10^{-6}) = 5.9 < 7$

5.

a.

$pH = -log([H_3O^+]) = -log(0.15) = 0.82$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.82 = 13$

b.

$pOH = -log([OH^-]) = -log(0.03) = 2$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 2 = 10$

c.

$pH = -log([H_3O^+]) = -log(2.3 \times 10^{-3}) = 2.6$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 2.6 = 11$

d.

$pOH = -log([OH^-]) = -log(9.78 \times 10^{-2}) = 1.01$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.01 = 13.0$

e.

$pH = -log([H_3O^+]) = -log(0.00017) = 3.8$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 3.8 = 10$

f.

$pH = -log([H_3O^+]) = -log(5.78) = -0.762$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - (-0.762) = 14.8$

6.

a. $25.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{2.3 \times 10^{-2}\,mol}{1\,L} \times \frac{1}{100\,mL \times \frac{1\,L}{1{,}000\,mL}} = 0.060\,M\,HCl$

$pH = -log([H_3O^+]) = -log(0.060) = 1.22$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 1.22 = 12.78$

b. $5.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{1.87\,mol}{1\,L} \times \frac{1}{125\,mL \times \frac{1\,L}{1{,}000\,mL}} = 7.5 \times 10^{-2}\,M\,NaOH$

$pOH = -log([OH^-]) = -log(7.5 \times 10^{-2}) = 1.1$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.1 = 12.9$

c. $5.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{5.98\,mol}{1\,L} \times \frac{1}{100\,mL \times \frac{1\,L}{1{,}000\,mL}} = 0.20\,M\,HCl$

$pH = -log([H_3O^+]) = -log(0.20) = 0.70$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.70 = 13.3$

d. $25.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{3.7\,mol}{1\,L} \times \frac{1}{250\,mL \times \frac{1\,L}{1{,}000\,mL}} = 0.370\,M\,HNO_3$

$pH = -log([H_3O^+]) = -log(0.370) = 0.432$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 0.432 = 13.568$

e. $35.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.046\,mol}{1\,L} \times \frac{1}{500\,mL \times \frac{1\,L}{1{,}000\,mL}} = 3 \times 10^{-3}\,M\,HI$

$pH = -log([H_3O^+]) = -log(3 \times 10^{-3}) = 2.52$

$pH + pOH = 14 \rightarrow pOH = 14 - pH = 14 - 2.52 = 11.48$

f. $15.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.0087\,mol}{1\,L} \times \frac{1}{125\,mL \times \frac{1\,L}{1{,}000\,mL}} = 5.20 \times 10^{-4}\,M\,KOH$

$pOH = -log([OH^-]) = -log(5.20 \times 10^{-4}) = 3.28$

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 3.28 = 10.72$

7. $[H^+] = 10^{-pH} = 10^{-1.5} = 3.2 \times 10^{-2}\,M$

8.

a. $[H^+] = 10^{-11.4} = 3.98 \times 10^{-12}\,M$

b. $[H^+] = 10^{-6.5} = 3.2 \times 10^{-7}\,M$

c. $[H^+] = 10^{-3.5} = 3.2 \times 10^{-4}\,M$

d. $[H^+] = 10^{-8.5} = 3.2 \times 10^{-9}\,M$

e. $[H^+] = 10^{-4.2} = 6.3 \times 10^{-5}\,M$

9. 2.9 mg HCl

$[H^+] = 10^{-pH} = 10^{-3.50} = 3.1622 \times 10^{-4}\,M$

$$x\,mg\,HCl \times \frac{1\,g\,HCl}{1{,}000\,mg\,HCl} \times \frac{1\,mol\,HCl}{36.46\,g\,HCl} \times \frac{1}{250\,mL\,H_2O \times \frac{1\,L}{1{,}000\,mL\,H_2O}} = 3.1622 \times 10^{-4}\,M\,HCl \rightarrow \frac{x\,mol\,HCl}{9115\,L\,HCl} = 3.1622 \times 10^{-4}\,M\,HCl \rightarrow x\,mol\,HCl = 3.1622 \times 10^{-4}\,M \times 9115\,L\,HCl \rightarrow x\,mol\,HCl = 2.9\,mol\,HCl \rightarrow x = 2.9$$

10. To prepare the stock solution, $2.11 \times 10^{-2}\,L$ of $0.500\,M\,NaOH$ solution is required.

$$\frac{0.03162\,mol\,NaOH}{1\,L\,NaOH} \times \frac{1\,L\,NaOH}{0.5\,mol\,NaOH} \times 0.333\,L = 2.11 \times 10^{-2}\,g\,NaOH.$$

$$[OH^-] = 10^{-1.5} = 0.03162\,M$$

$$pH + pOH = 14 \rightarrow pOH = 14 - 12.50 = 1.5$$

16.4: The pH Scale

16.5: Strong Acids and Bases

16.6: Weak Acids

16.7: Weak Bases

16.8: Relationship Between Ka and Kb

16.9: Acid-Base Properties of Salt Solutions

16.10: Acid-Base Behavior and Chemical Structure

Conceptual Problems

1. Several factors affect the relative strengths of acids and bases. For each pair, identify the most important factor in determining which is the stronger acid or base in aqueous solution.
   a. $CH_3CCl_2CH_2CO_2H$ versus $CH_3CH_2CH_2CO_2H$
   b. CH_3CO_2H versus CH_3CH_2OH
   c. $HClO$ versus $HBrO$
   d. $CH_3C(=O)NH_2$ versus $CH_3CH_2NH_2$
   e. H_3AsO_4 versus H_3AsO_3
2. The stability of the conjugate base is an important factor in determining the strength of an acid. Which would you expect to be the stronger acid in aqueous solution—$C_6H_5NH_3^+$ or NH_4^+? Justify your reasoning.
3. Explain why H_2Se is a weaker acid than HBr.
4. Arrange the following in order of decreasing acid strength in aqueous solution: H_3PO_4, $CH_3PO_3H_2$, and $HClO_3$.
5. Arrange the following in order of increasing base strength in aqueous solution: CH_3S^-, OH^-, and CF_3S^-.

6. Arrange the following in order of increasing acid strength in aqueous solution: $HClO_2$, HNO_2, and HNO_3.
7. Do you expect H_2SO_3 or H_2SeO_3 to be the stronger acid? Why?
8. Give a plausible explanation for why CF_3OH is a stronger acid than CH_3OH in aqueous solution. Do you expect $CHCl_2CH_2OH$ to be a stronger or a weaker acid than CH_3OH? Why?
9. Do you expect Cl_2NH or NH_3 to be the stronger base in aqueous solution? Why?

Conceptual Answers

1.

a. The most important factor in determining the stronger acid is considering the inductive effect. Chlorine is an electron-withdrawing group. It pulls electron density away from the compound by means of the inductive effect through the sigma bond. In considering the conjugate base of $CH_3CCl_2CH_2CO_2H$, Chlorine absorbs some of the electron density or excess negative charge on the oxygen atom. This causes the C bonded to the attached Chlorine atoms to be partially positive. The conjugate base of $CH_3CCl_2CH_2CO_2H$ is more stable, thus more acidic than the conjugate base of $CH_3CH_2CH_2CO_2H$.

b. The most important factor in determining the stronger acid is knowing the pK_a values for functional groups. The pK_a of alcohol is about 16 while the pK_a of a carboxylic acid is about 5. Therefore, CH_3CO_2H is more acidic than CH_3CH_2OH.

c. The most important factor in determining the stronger acid is electronegativity. The chlorine atom is more electronegative than the bromine atom, therefore $HClO$ is more acidic than $HBrO$.

d. The most important factor in determining the stronger acid is considering resonance. The $CH_3C(=O)NH_2$ has a resonance which increases the stability of the conjugate base (therefore increasing acidity) because the negative charge can be delocalized. Thus, $CH_3C(=O)NH_2$ is more acidic than $CH_3CH_2NH_2$.

e. The most important factor in determining the stronger acid is considering oxidation states on the central nonmetal. H_3AsO_4 has an oxidation state of +5 which is larger and thus more acidic than H_3AsO_3 which has an oxidation state of +3.

$CF_3S^- < CH_3S^- < OH^-$ (strongest base)

NH_3; Cl atoms withdraw electron density from N in Cl_2NH.

2. It is expected that the stronger acid is $C_6H_5NH_3^+$ because in considering the conjugate base the lone pair of electrons on nitrogen is involved in resonance, hence the molecule is stable.

3. H_2Se is a weaker acid than HBr because Br is more electronegative than Se thus more stable.

4. $HClO_3 > CH_3PO_3H_2 > H_3PO_4$

This is because H_3PO_4 is a polyprotic acid which contains more than one ionizable proton, and the protons are lost in a stepwise manner. The fully protonated species is always the strongest acid because it is easier to remove a proton from a neutral molecule than from a negatively charged ion. Thus, acid strength decreases with the loss of subsequent protons, and, correspondingly, the pK_a increases which indicate it is the most basic. The conjugate base of ClO^{3-} has a much smaller charge to volume ratio, thus most stable and acidic.

5. $CF_3S^- < CH_3S^- < OH^-$

CF_3S^- is the most acidic because of the three electronegative Fluorines. OH^- is the strongest base in water. Thus, CH_3S^- is in between these aqueous solutions.

6. $HNO_2 < HClO_2 < HNO_3$

HNO_3 has resonance stabilization, therefore it is the most acidic. Between $HClO_2$ and HNO_2, Cl is the most electronegative therefore $HClO_2$ is more acidic than HNO_2.

7. I expect H_2SO_3 to be the stronger acid because it is more electronegative or has greater attraction which means it'll be less inclined to share their electrons with a proton.

8. CF_3OH is a stronger acid than CH_3OH in aqueous solution because F is more electronegative than H.

9. It would be expected that NH_3 be a stronger base than Cl_2NH because it is electronegative due to the two Cl atoms.

16.11: Lewis Acids and Bases

Problems

1. Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:

a. NH_3
b. Ag^+
c. Ni^{2+}
d. Pt^{4+}
e. H_2O
f. SO_2

2. Explain why SiF_4 can act as a Lewis Acid.

3. Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:

a. $[Fe(CN)_6]^{3-}$
b. $[Ni(NH_3)_6]^{2+}$
c. $CdBr_4^{2-}$

4. What is the product of the reaction of $CO_2 + OH^- \rightarrow$?

5. In the reactions below, which is the Lewis Acid and/or which is the Lewis Base?

a. $NH_3 + H^+ \rightarrow NH_4^+$
b. $H_2O + H^+ \rightarrow H_3O^+$

6. In the complex ion, $[PtCl_6]^{2-}$ which is the Lewis Acid and which is the Lewis base?

7. The reaction of $AgCl$ + NH_3 produces what complex ion?

Solutions

1.

a. NH_3 is a lewis base because nitrogen has a lone pair of electrons to "donate."

b. Ag^+ is a lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.

c. Ni^+ is a lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.

d. Pt^{4+} is a lewis acid because it has an unfilled octet and thus is able to accept a pair of electrons.

e. H_2O is a lewis base because oxygen has two lone pairs of electrons to "donate."

f. SO_2 is a lewis acid because sulfur has an unfilled octet and thus is able to accept a pair of electrons.

2. \(SiF_4\) has a central Silicon Atom which can expand its octet to 12 (compared to the typical 8) so that it forms \([SiF_6]^{2-}\).

3.

a. Lewis Acid: Fe^{3+}, Lewis Base: CN^-
b. Lewis Acid: Ni^{2+}, Lewis Base: NH_3
c. Lewis Acid: Cd^{2+}, Lewis Base: Br^-

4. This reaction forms a bicarbonate ion. $CO_2 + OH^- \rightarrow O--COH=O$.

5.

a. Lewis Acid: H^+, Lewis Base: NH_3

b. Lewis Acid: H^+, Lewis Base: H_2O

6. Pt^{4+} is the Lewis acid and Cl^- is the Lewis base.

7.

$$AgCl + 2\,NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^- \tag{3.E.10}$$

Conceptual Problems

1. Construct a table comparing how OH^-, NH_3, H_2O, and BCl_3 are classified according to the Arrhenius, the Brønsted–Lowry, and the Lewis definitions of acids and bases
2. Describe how the proton (H^+) can simultaneously behave as an Arrhenius acid, a Brønsted–Lowry acid, and a Lewis acid.
3. Would you expect aluminum to form compounds with covalent bonds or coordinate covalent bonds? Explain your answer.
4. Classify each compound as a Lewis acid or a Lewis base and justify your choice.
   a. $AlCl_3$
   b. CH_3N
   c. IO_3^-
5. Explain how a carboxylate ion (RCO_2^-) can act as both a Brønsted–Lowry base and a Lewis base.

Conceptual Answers

1.

	Arrhenius Acid	Arrhenius Base	Brønsted–Lowry Acid	Brønsted–Lowry Base	Lewis Acid	Lewis Base
OH^-		X		X		X
NH_3				X		X
H_2O	X	X	X	X		X
BCl_3					X	

An Arrhenius acid is a molecule that when dissolved in water it will donate an H^+ in solution.

An Arrhenius base is a molecule that when dissolved in water it will donate an OH^- in solution.

A Brønsted–Lowry acid is a molecule that when dissolved in a solution it will donate an H^+ in solution.

A Brønsted–Lowry base is a molecule that when dissolved in a solution it will donate an atom or ion capable of accepting or bonding to a free proton in solution.

A Lewis acid is an atom or molecule that accepts an electron pair.

A Lewis base is an atom or molecule that donates an electron pair.

2.

The proton (H^+) can simultaneously behave as an Arrhenius acid because when it is dissolved in water it will donate itself. $H^+ + H_2O \rightleftharpoons H_3O^+$

The proton (H^+) can simultaneously behave as a Brønsted–Lowry acid because when it is dissolved in solution it will donate itself.

$H^+ + B^- \rightleftharpoons HB$

The proton (H^+) can simultaneously behave as a Lewis acid as it can accept an electron pair.

$H^+ + B^- \rightleftharpoons HB$

3. It is expected that Aluminum forms a coordinate covalent bond as it can participate in a Lewis acid and a Lewis base interaction. For example $Al^{3+} + H_2O \rightleftharpoons [Al(OH_2)_6]^{3+}$

4.

a. $AlCl_3$ is a Lewis acid as Al can accept an electron pair.

b. CH_3N is a Lewis base as N can donate an electron pair.

c. IO_3^- is a Lewis base as I can donate an electron pair.

5. The carboxylate ion (RCO_2^-) can act as Brønsted–Lowry base because when dissolved in a solution the electron rich O is capable of accepting a proton. The carboxylate ion (RCO_2^-) can act as a Lewis base because the electron rich O can donate an electron pair.

Numerical Problems

1. In each reaction, identify the Lewis acid and the Lewis base and complete the reaction by writing the products(s).

a. $(CH_3)_2O + AlCl_3$

b. $SnCl_4 + 2\ Cl^-$

2. Use Lewis dot symbols to depict the reaction of BCl_3 with dimethyl ether [$(CH_3)_2O$]. How is this reaction similar to that in which a proton is added to ammonia?

Answer

1.

a. The Lewis acid is $AlCl_3$ and the Lewis base is $(CH_3)_2O$.

$$(CH_3)_2O + AlCl_3 \rightleftharpoons AlCl_3 \cdot O(CH_3)_2$$

b. The Lewis acid is $SnCl_4$ and the Lewis base is Cl^-.

$$SnCl_4 + 2\,Cl^- \rightleftharpoons SnCl_6^{2-}$$

2.

$$BCl_3 + (CH_3)_2O \rightleftharpoons BCl_3 \cdot O(CH_3)_2$$

This reaction is similar to that in which a proton is added to ammonia as it also involves a Lewis acid and a Lewis base interaction.

3.E: Acid–Base (more practice questions with answers) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

4: Aqueous Ionic Equilibrium

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4.1: 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 4.1.1). A solution of acetic acid (CH_3COOH and sodium acetate 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 ($NH_3(aq)$) and ammonium chloride ($NH_4Cl(aq)$).



Figure 4.1.1: (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:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2^-(aq)$$

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:

$$H_3O^+(aq) + CH_3CO_2^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 4.1.2).

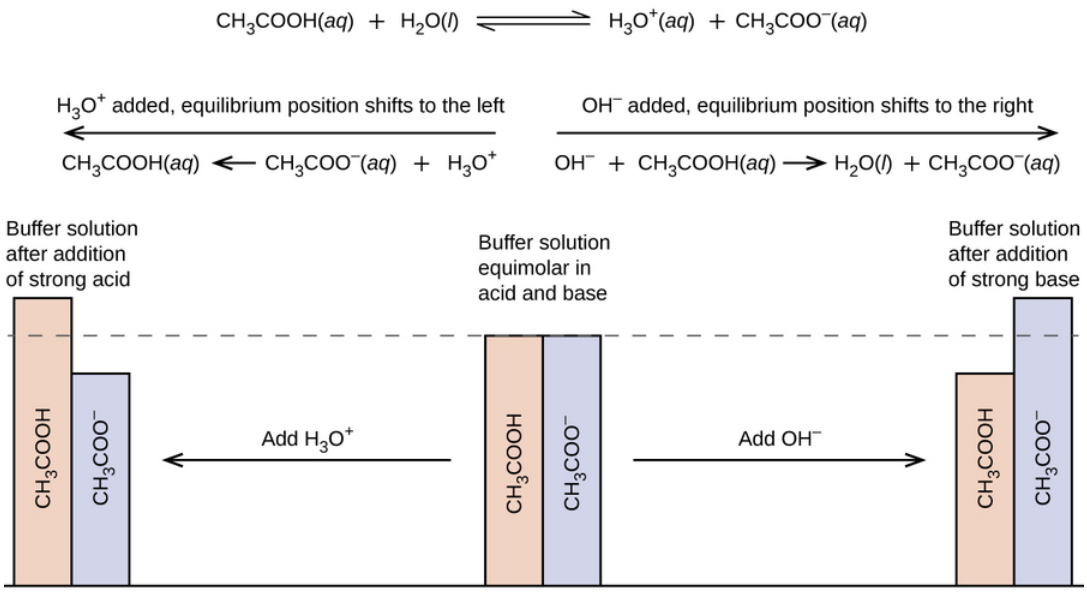


Figure **4.1.2**: This diagram shows the buffer action of these reactions.

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:

$$\mathbf{NH_4^+}(aq) + \mathbf{OH^-}(aq) \longrightarrow \mathbf{NH_3}(aq) + \mathbf{H_2O}(l)$$

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:

$$\mathbf{H_3O^+}(aq) + \mathbf{NH_3}(aq) \longrightarrow \mathbf{NH_4^+}(aq) + \mathbf{H_2O}(l)$$

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 4.1.1: pH Changes in Buffered and Unbuffered Solutions

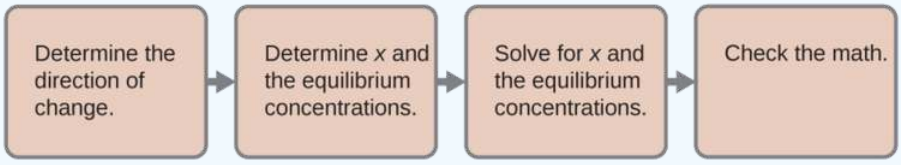
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

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^+, $\mathbf{CH_3CO_2^-}$, and CH_3CO_2H is:

$$\mathbf{CH_3CO_2H}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{H_3O^+}(aq) + \mathbf{CH_3CO_2^-}(aq)$$

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:

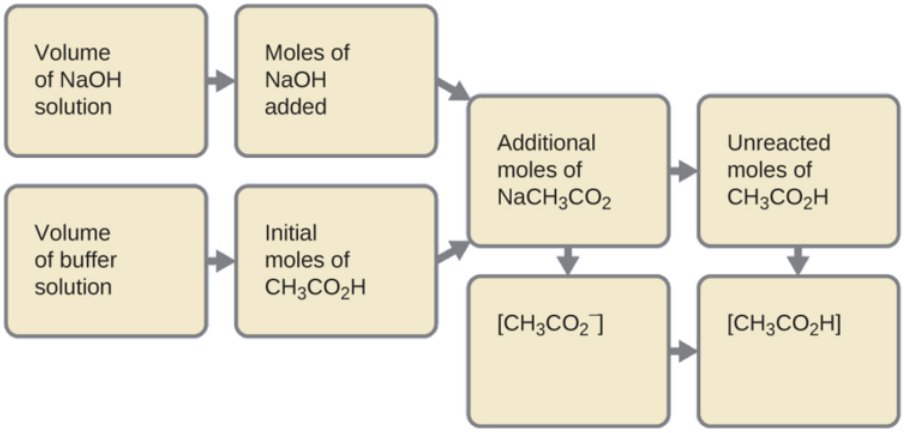
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

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:

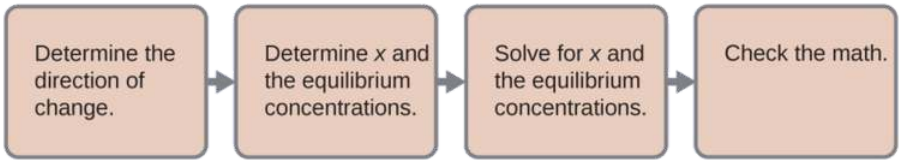
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

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 4.1.1

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 **4.1.3**). 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 **4.1.3**: 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 **4.1.4** 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.

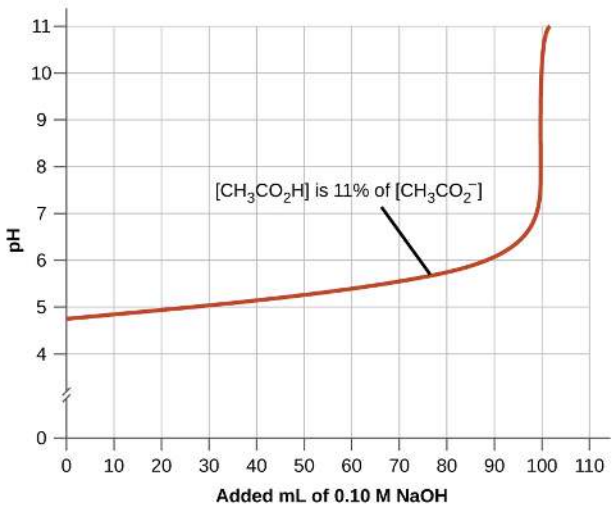


Figure **4.1.4**: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2^-] = 0.10\ M$.

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

- $pK_a = -\log K_a$
- $pK_b = -\log K_b$
- $\mathrm{pH} = pK_a + \log \frac{[A^-]}{[HA]}$

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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4.2: 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 4.2.1: 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 **4.2.1**. 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 $\mathbf{pH}$:

$$\mathbf{pH} = -\log([\mathbf{H_3O^+}]) \tag{4.2.1}$$

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:

$$[H_3O^+] = [OH^-\ ],\ [H_3O^+] = K_w = 1.0 \times 10^{-14};\ [H_3O^+] = 1.0 \times 10^{-7}$$

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

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:

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

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

then using the definition of $\boldsymbol{pOH}$ and its relationship to $\boldsymbol{pH}$ in room temperature aqueous solutios (Equation 4.2.1):

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

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

(a) X = 0 mL

$$[H_3O^+] = \frac{\text{n}(H^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL}} = 0.1\ M$$

then using the definition of $\boldsymbol{pH}$ (Equation 4.2.1):

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

(b) X = 12.50 mL

$$[H_3O^+] = \frac{\text{n}(H^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times 12.50\ \text{mL}}{25.00\ \text{mL} + 12.50\ \text{mL}} = 0.0333\ M$$

then using the definition of $\boldsymbol{pH}$ (Equation 4.2.1):

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

(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 4.2.1):

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

Exercise 4.2.1

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 **4.2.1**, we calculated pH at four points during a titration. Table **4.2.1** shows a detailed sequence of changes in the pH of a strong acid and a weak acid in a titration with NaOH.

Table **4.2.1**: 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 **4.2.1** 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 **4.2.1**, 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 **4.2.1** and Figure **4.2.1**).

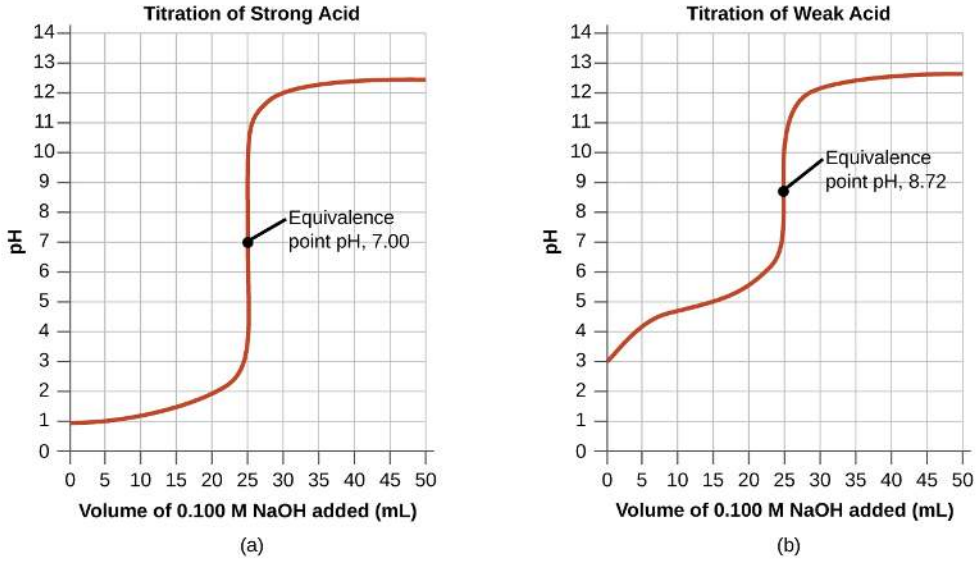


Figure 4.2.1: (a) The titration curve for the titration of 25.00 mL of 0.100 M HCl (strong acid) with 0.100 M NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) has an equivalence 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 4.2.1 gives the pH values during the titration, Figure 4.2.1*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:

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

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

Example 4.2.2: Titration of a Weak Acid with a Strong Base

The titration curve shown in Figure 4.2.1*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:

$$CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O$$

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:

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

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

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

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

$$K_b = \frac{[CH3CO2H][OH-]}{[CH3CO2-]}$$

$$K_a = \frac{[CH3CO2-][H+]}{[CH3CO2H]}, \text{ so } \frac{[CH3CO2H]}{[CH3CO2-]} = \frac{[H^+]}{K_a}.$$

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

$$K_b = \frac{[H^+][OH^-]}{K_a} \tag{4.2.2}$$

$$= \frac{K_w}{K_a} \tag{4.2.3}$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \tag{4.2.4}$$

$$= 5.6 \times 10^{-10} \tag{4.2.5}$$

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 4.2.2

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:

$$\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]} = \frac{[\text{substance with yellow color}]}{[\text{substance with red color}]} = \frac{K_a}{[\mathrm{H_3O^+}]} \tag{4.2.6}$$

Equation 4.2.6 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:

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \tag{4.2.7}$$

$$\log\left(\frac{[H_3O^+]}{K_a}\right) = \log\left(\frac{[HIn]}{[In^-]}\right) \tag{4.2.8}$$

$$\log([H_3O^+]) - \log(K_a) = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{4.2.9}$$

$$-pH + pK_a = -\log\left(\frac{[In^-]}{[HIn]}\right) \tag{4.2.10}$$

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right) \tag{4.2.11}$$

or in general terms

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{4.2.12}$$

Equation 4.2.12 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 **4.2.2** presents several indicators, their colors, and their color-change intervals.

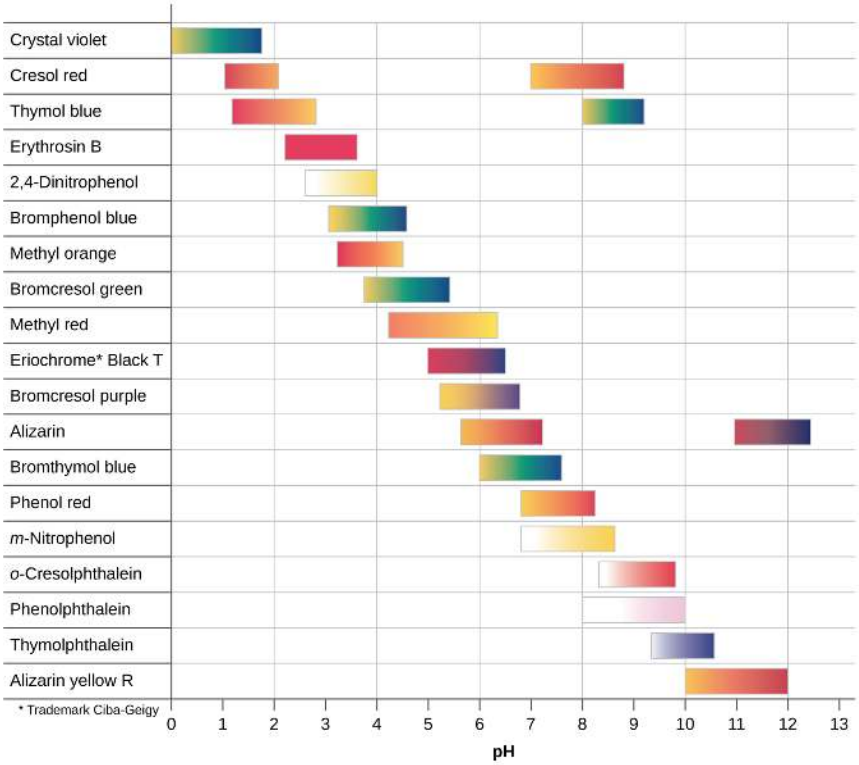


Figure 4.2.2: This chart illustrates the ranges of color change for several acid-base indicators.

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 4.2.3. 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.

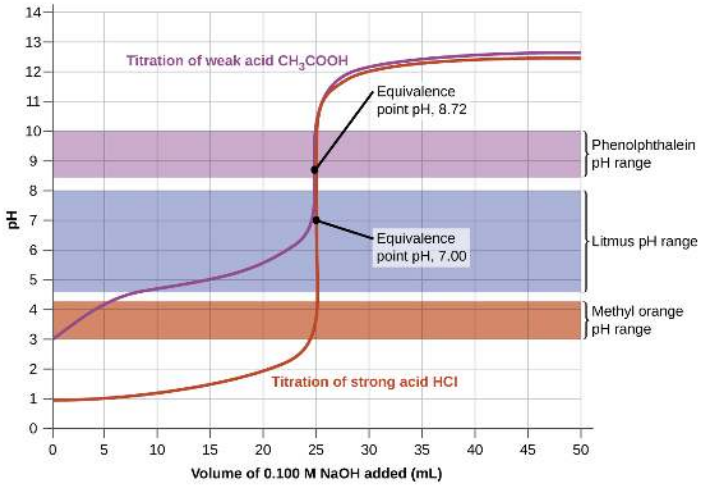


Figure **4.2.3**: The graph shows a titration curve for the titration of 25.00 mL of 0.100 M CH_3CO_2H (weak acid) with 0.100 M NaOH (strong base) and the titration curve for the titration of HCl (strong acid) with NaOH (strong base). The pH ranges for the color change of phenolphthalein, litmus, and 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 **4.2.2** 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 **4.2.2** 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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4.3: pH and pOH calculation of weak acids and bases, polyprotic acids and bases titration curves

Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure 4.3.1*a* shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in Figure 4.3.1*b*. As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

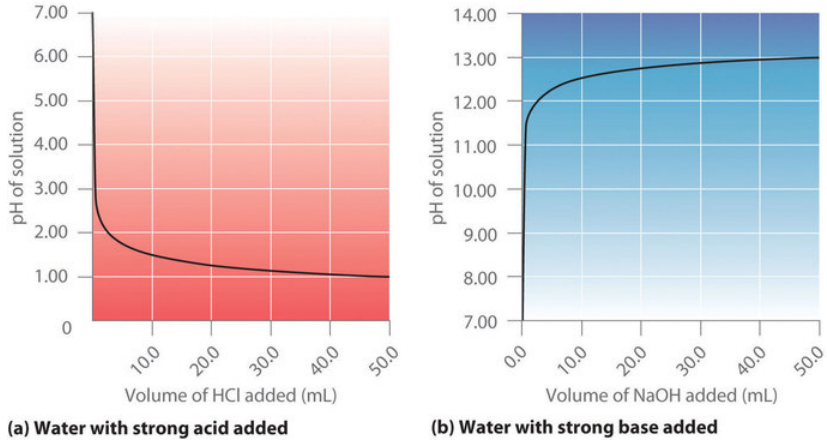


Figure 4.3.1: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M *NaOH*. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial [H^+] is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H+ because of the neutralization reaction (Figure 4.3.2*a*):

$$OH^- + H^+ \rightleftharpoons H_2O.$$

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$\begin{aligned} moles\ of\ base &= (volume)_b(molarity)_b V_b M_b = moles\ of\ acid \\ &= (volume)_a(molarity)_a = V_a M_a \end{aligned} \tag{4.3.1}$$

If 0.20 M **NaOH** is added to 50.0 mL of a 0.10 M solution of **HCl**, we solve for V_b:

$$V_b(0.20 Me) = 0.025 L = 25 mL$$

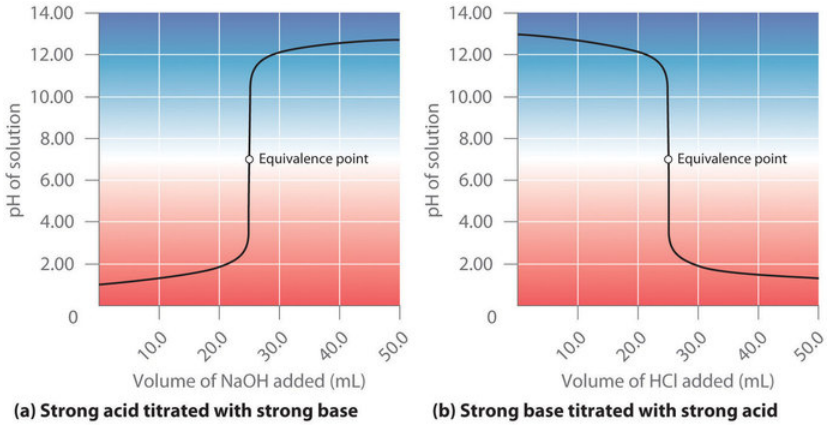


Figure **4.3.2**: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M **NaOH** is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M **HCl** is slowly added to 50.0 mL of 0.10 M ***NaOH***, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of **NaOH** solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more **NaOH** produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M ***NaOH***.

As shown in Figure **4.3.2*b***, the titration of 50.0 mL of a 0.10 M solution of **NaOH** with 0.20 M **HCl** produces a titration curve that is nearly the mirror image of the titration curve in Figure **4.3.2*a***. The pH is initially 13.00, and it slowly decreases as **HCl** is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M **HCl**.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

✔ Example **4.3.1**: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M **NaOH** has been added to 50.00 mL of 0.100 M **HCl**.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of $\mathrm{H^+}$ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00 \cancel{mL}\left(\frac{0.100\ mmol\ HCl}{\cancel{mL}}\right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90 \cancel{mL}\left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}}\right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus $\mathrm{H^+}$ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of $\mathrm{OH^-}$ to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess $\mathrm{H^+}$ is 5.00 mmol − 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of $\mathrm{H^+}$ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[\mathrm{H^+}] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

? Exercise 4.3.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133M$ solution of $NaOH$.

Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, [H^+] of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, [\(H^+] is less than [HA]. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure 4.3.3*a* shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure 4.3.2. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

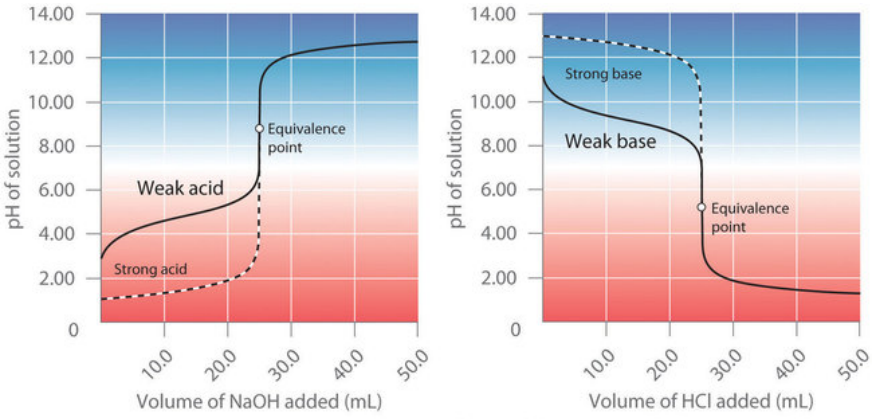


Figure **4.3.3**: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M **NaOH** is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M **HCl** with 0.200 M **NaOH** is shown as a dashed line. (b) As 0.200 M **HCl** is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M **NaOH** with 0.200 M **HCl** is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in Figure **4.3.3***a* was created by calculating the starting pH of the acetic acid solution before any **NaOH** is added and then calculating the pH of the solution after adding increasing volumes of $NaOH$. The procedure is illustrated in the following subsection and Example **4.3.2** for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H\,(aq) \rightleftharpoons H^+\,(aq) + CH_3CO_2{}^-$$

table of concentrations for the ionization of 0.100 M acetic acid

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	−x	+x	+x
final	0.100 − x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$
$$= \frac{(x)(x)}{0.100 - x}$$
$$\approx \frac{x^2}{0.100}$$
$$\approx 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$



pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M **NaOH** to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure **4.3.3**). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{4.3.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[H^+]$ of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of CH_3CO_2H in the original solution and the amount of OH^- in the **NaOH** solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}\ (0.100\ mmol(CH_3CO_2H)/\cancel{mL}) = 5.00\ mmol(CH_3CO_2H)$$

The **NaOH** solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H − 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

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

ICE table

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2{}^-]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[H^+]$ at equilibrium following the addition of $NaOH$, we must first calculate $[CH_3CO_2H]$ and $[CH_3CO_2{}^-]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$[CH_3CO_2^-] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

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

$$[H^+] = \frac{K_a\,[CH_3CO_2H]}{[CH_3CO_2^-]} = \frac{(1.72 \times 10^{-5})\,(7.27 \times 10^{-2}\ M)}{(1.82 \times 10^{-2})} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[H^+]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure **4.3.3***a*, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example **4.3.2**, we calculate another point for constructing the titration curve of acetic acid.



pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 4.3.2

What is the pH of the solution after 25.00 mL of 0.200 M **NaOH** is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.

B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.

C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.

D. Calculate K_b using the relationship $K_w = K_aK_b$. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}-\text{mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[CH_3CO_2] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

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

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{4.3.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^-$$

completed table of concentrations

	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 4.3.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} \tag{4.3.4}$$

Substituting the expressions for the final values from the ICE table into Equation 4.3.4 and solving for x:

$$\frac{x^2}{0.0667} = 5.80 \times 10^{-10}$$

$$x = \sqrt{(5.80 \times 10^{-10})(0.0667)}$$

$$= 6.22 \times 10^{-6}$$

Thus $[OH^-] = 6.22 \times 10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure 4.3.3*a*). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce OH^-.

? Exercise 4.3.2

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

9.23

As shown in part (b) in Figure **4.3.3**, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure **4.3.4** illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

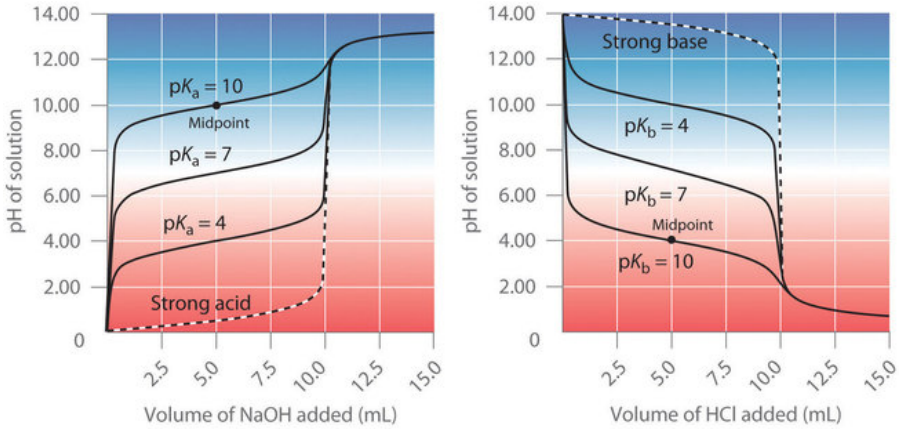


Figure **4.3.4**: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M **NaOH** added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M **HCl** added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures **4.3.4***a* and **4.3.4***b* for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A−]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH \tag{4.3.5}$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure **4.3.4** for the weakest acid where we see that the midpoint for pK_a = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the

overall titration curve shows well-resolved "steps" corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 4.3.5 and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_a2. Because HPO_4^{2-} is such a weak acid, pK_a3 has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

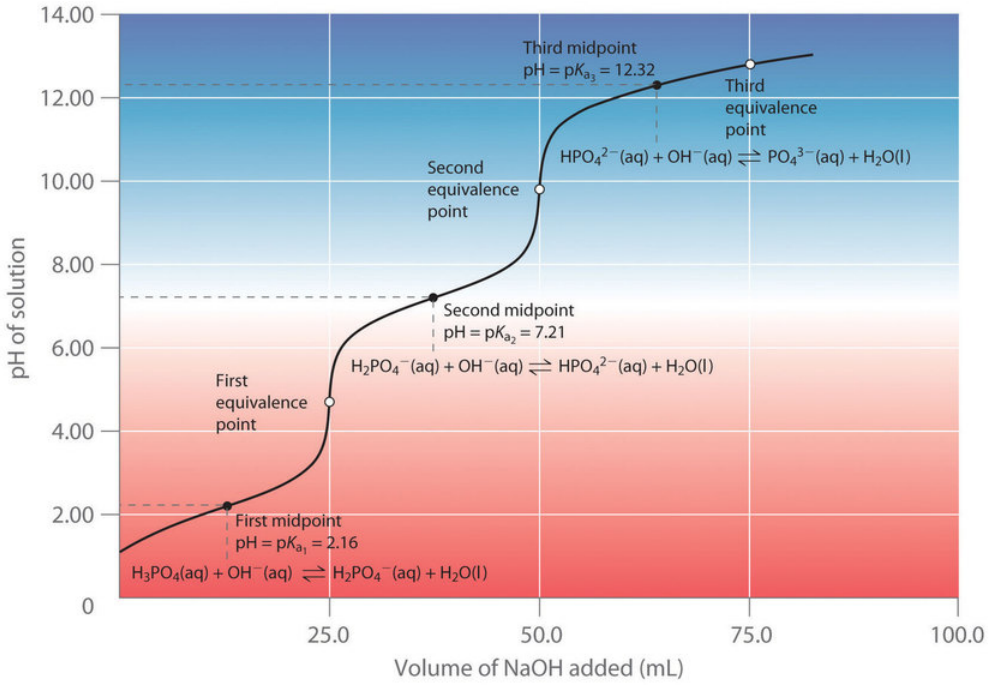
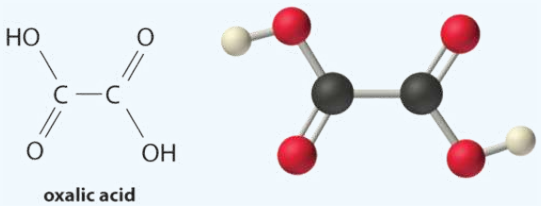


Figure 4.3.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 4.3.5. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table E1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

✔ Example 4.3.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid (HO_2CCO_2H), a diprotic acid (abbreviated as H_2ox). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($O_2CCO_2^{2-}$, abbreviated ox^{2-}).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine [H+] and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\,\cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right) = 5.10\ mmol\ H_2ox$$

$$55.00\,\cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right) = 6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of OH^- to react with Hox−, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

Solutions to Example 17.3.3

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	−5.10 mmol	−5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	−1.50 mmol	−1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 4.3.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$[Hox^-] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$[ox^{2-}] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{[ox^{2-}]\,[H^+]}{[Hox^-]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$[H^+] = \frac{K_{a2}[Hox^-]}{[ox^{2-}]} = \frac{(1.6 \times 10^{-4})(2.32 \times 10^{-2})}{(9.68 \times 10^{-3})} = 3.7 \times 10^{-4}\ M$$

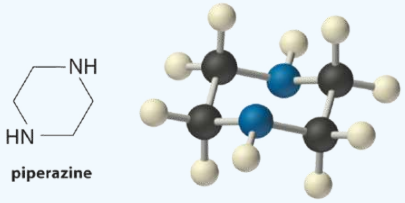
So

$$pH = -\log[H^+] = -\log(3.7 \times 10^{-4}) = 3.43$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

? Exercise 4.3.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites ("worms") in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog's stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$HIn\,(aq) \rightleftharpoons H^+\,(aq) + In^-\,(aq)$$

where the protonated form is designated by HIn and the conjugate base by In^-. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \tag{4.3.6}$$

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure 4.3.6). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.

- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure **4.3.6**: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure **4.3.7** shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

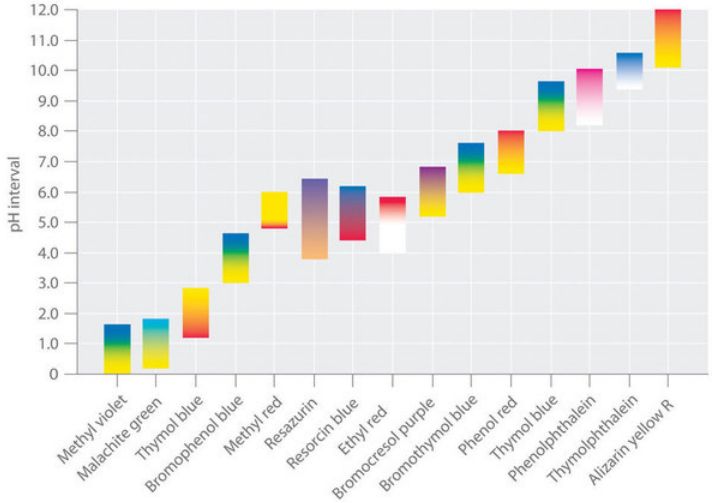


Figure **4.3.7**: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In− increases, the color of the solution slowly changes from the characteristic color of HIn to that of In−. As we will see later, the [In−]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure **4.3.8**. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the **HCl** titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of **NaOH** has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether

methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the **HCl** titration, the phenolphthalein indicator will turn pink when about 50 mL of **NaOH** has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of **NaOH** will therefore cause the methyl red indicator to change color, resulting in a huge error.

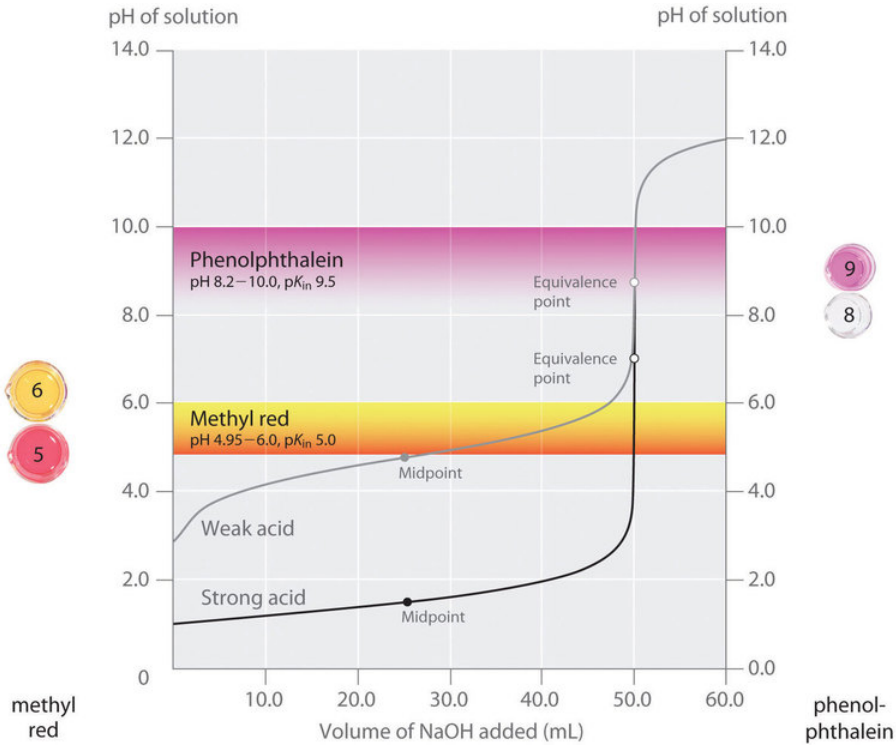


Figure **4.3.8**: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M ***NaOH***. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure **4.3.9**).

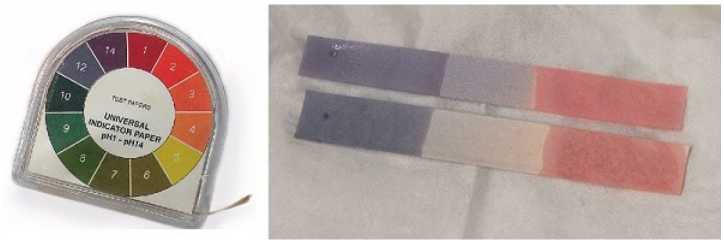


Figure **4.3.9**: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



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

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

4.3: pH and pOH calculation of weak acids and bases, polyprotic acids and bases titration curves is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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4.4: Acid rain

5.12: Enthalpy

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4.5: Solubility Equilibria and the Solubility Product Constant (Ksp)

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{4.5.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[Ca^{2+}]^3[PO_4^{3-}]^2}{[Ca_3(PO_4)_2]} \tag{4.5.2}$$

$$[Ca_3(PO_4)_2]K = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{4.5.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table **4.5.1**, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 4.5.2 and 4.5.3, changes in pH can affect the solubility of a compound as discussed later.

> *As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table **4.5.1**: Solubility Products for Selected Ionic Substances at 25°C

.

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2 \cdot 3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates				$MgC_2O_4 \cdot 2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		
Chlorides				Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}		**Sulfates**		
Chromates				Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
Fluorides				**Sulfides**		
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
Hydroxides				PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				

*These contain the Hg_2^{2+} ion.



Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 4.5.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)\cdot H_2O$, also written as $CaC_2O_4\cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.

B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l) \quad K_{sp} = [Ca^{2+}][ox^{2-}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine [Ca^{2+}] and [ox^{2-}] at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2) \cdot \text{H}_2\text{O}$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04 \times 10^{-6}\ \text{mol}\ \text{Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right) = 5.04 \times 10^{-5}\ \text{mol/L} = 5.04 \times 10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp} = [Ca^{2+}][ox^{2-}] = (5.04 \times 10^{-5})(5.04 \times 10^{-5}) = 2.54 \times 10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

? Exercise 4.5.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calcite its K_{sp}.

Answer

4.5×10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example **4.5.1**. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 4.5.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.
B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation **4.5.2**) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	$+3x$	$+2x$
final	pure solid	$3x$	$2x$

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \quad (4.5.4)$$

$$2.07 \times 10^{-33} = 108x^5 \quad (4.5.5)$$

$$1.92 \times 10^{-35} = x^5 \quad (4.5.6)$$

$$1.14 \times 10^{-7}\ \text{M} = x \quad (4.5.7)$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is 2*x* and 3*x*, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

? Exercise 4.5.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg



Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

> *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure **4.5.1**, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.

- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

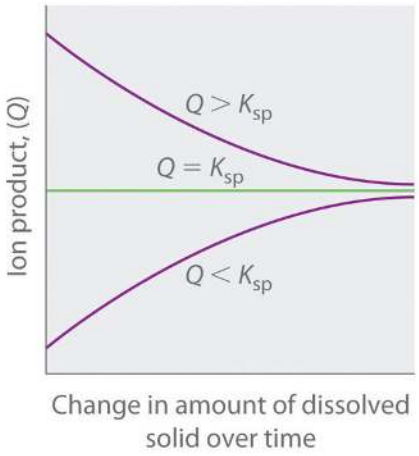


Figure **4.5.1**: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium ($Q = K_{sp}$). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until $Q = K_{sp}$. If $Q = K_{sp}$, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 4.5.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.

B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).

C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}}\right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5} \text{ mol } Ba^{2+}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 2.9 \times 10^{-4} \text{ M } Ba^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles } SO_4^{2-} = 10.0 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)\left(\frac{0.0020 \text{ mol}}{1 \text{ L}}\right) = 2.0 \times 10^{-5} \text{ mol } SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5} \text{ mol } SO_4^{2-}}{110 \text{ mL}}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 1.8 \times 10^{-4} \text{ M } SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

? Exercise 4.5.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)



Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of

$Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7}\ M\ Ca^{2+}$ and $2 \times (1.14 \times 10^{-7}\ M) = 2.28 \times 10^{-7}\ M\ PO_4^{3-}$, according to the stoichiometry shown in Equation 4.5.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 4.5.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *The common ion effect usually **decreases** the solubility of a sparingly soluble salt.*

Example 4.5.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again $+3x$, and the change in $[PO_4^{3-}]$ is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	Ca3(PO4)2	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07 \times 10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ M \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 4.5.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 4.5.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

4.5: Solubility Equilibria and the Solubility Product Constant (Ksp) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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4.6: Solubility and Common ion effect

Learning Objectives

- Recognize common ions from various salts, acids, and bases.
- Calculate concentrations involving common ions.
- Calculate ion concentrations involving chemical equilibrium.

The common-ion effect is used to describe the effect on an equilibrium involving a substance that adds an ion that is a part of the equilibrium.

Introduction

The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, these salts contribute to the concentration of the common ion. Contributions from all salts must be included in the calculation of concentration of the common ion. For example, a solution containing sodium chloride and potassium chloride will have the following relationship:

$$[Na^+] + [K^+] = [Cl^-] \tag{4.6.1}$$

Consideration of *charge balance* or *mass balance* or both leads to the same conclusion.

Common Ions

When **NaCl** and **KCl** are dissolved in the same solution, the Cl^- ions are *common* to both salts. In a system containing **NaCl** and **KCl**, the Cl^- ions are common ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$$

$$AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

For example, when **AgCl** is dissolved into a solution already containing **NaCl** (actually Na^+ and Cl^- ions), the Cl^- ions come from the ionization of both **AgCl** and **NaCl**. Thus, $[Cl^-]$ differs from $[Ag^+]$. The following examples show how the concentration of the common ion is calculated.

Example 4.6.1

What are $[Na^+]$, $[Cl^-]$, $[Ca^{2+}]$, and $[H^+]$ in a solution containing 0.10 M each of **NaCl**, $CaCl_2$, and **HCl**?

Solution

Due to the conservation of ions, we have

$$[Na^+] = [Ca^{2+}] = [H^+] = 0.10\ M$$

but

$$\begin{aligned}[Cl^-] = &\ 0.10 \text{ (due to NaCl)} \\ &+ 0.20 \text{ (due to } CaCl_2\text{)} \\ &+ 0.10 \text{ (due to HCl)} \\ = &\ 0.40\ M\end{aligned}$$

Exercise 4.6.1

John poured 10.0 mL of 0.10 M **NaCl**, 10.0 mL of 0.10 M **KOH**, and 5.0 mL of 0.20 M **HCl** solutions together and then he made the total volume to be 100.0 mL. What is $[Cl^-]$ in the final solution?

Solution

$$[Cl^-] = \frac{0.1\ M \times 10\ mL + 0.2\ M \times 5.0\ mL}{100.0\ mL} = 0.020\ M$$

Le Châtelier's Principle states that if an equilibrium becomes unbalanced, the reaction will shift to restore the balance. If a common ion is added to a weak acid or weak base equilibrium, then the equilibrium will shift towards the reactants, in this case the weak acid or base.

Example 4.6.2: Solubility of Lead Chloride

Consider the lead(II) ion concentration in this *saturated* solution of $PbCl_2$. The balanced reaction is

$$PbCl_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

Defining s as the concentration of dissolved lead(II) chloride, then:

$$[Pb^{2+}] = s$$

$$[Cl^-] = 2s$$

These values can be substituted into the solubility product expression, which can be solved for s:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \tag{4.6.2}$$

$$= s \times (2s)^2 \tag{4.6.3}$$

$$1.7 \times 10^{-5} = 4s^3 \tag{4.6.4}$$

$$s^3 = \frac{1.7 \times 10^{-5}}{4} \tag{4.6.5}$$

$$= 4.25 \times 10^{-6} \tag{4.6.6}$$

$$s = \sqrt[3]{4.25 \times 10^{-6}} \tag{4.6.7}$$

$$= 1.62 \times 10^{-2}\ mol\ dm^{-3} \tag{4.6.8}$$

The concentration of lead(II) ions in the solution is 1.62 x 10^{-2} M. Consider what happens if sodium chloride is added to this saturated solution. Sodium chloride shares an ion with lead(II) chloride. The chloride ion is **common** to both of them; this is the origin of the term "common ion effect".

Look at the original equilibrium expression again:

$$PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq)$$

What happens to that equilibrium if extra chloride ions are added? According to *Le* Châtelier, the position of equilibrium will shift to counter the change, in this case, by removing the chloride ions by making extra solid lead(II) chloride.

Of course, the concentration of lead(II) ions in the solution is so small that only a tiny proportion of the extra chloride ions can be converted into solid lead(II) chloride. The lead(II) chloride becomes even *less soluble*, and the concentration of lead(II) ions in the solution *decreases*. This type of response occurs with any sparingly soluble substance: it is less soluble in a solution which contains any ion which it has in common. This is the common ion effect.

Example 4.6.3

If an attempt is made to dissolve some lead(II) chloride in some 0.100 M sodium chloride solution instead of in water, what is the equilibrium concentration of the lead(II) ions this time? As before, define s to be the concentration of the lead(II) ions.

$$[Pb^{2+}] = s \tag{4.6.9}$$

The calculations are different from before. This time the concentration of the chloride ions is governed by the concentration of the sodium chloride solution. The number of ions coming from the lead(II) chloride is going to be tiny compared with the 0.100 M coming from the sodium chloride solution.

In calculations like this, it can be assumed that the concentration of the common ion is entirely due to the other solution. This simplifies the calculation.

So we assume:

$$[Cl^-] = 0.100\ M \tag{4.6.10}$$

The rest of the mathematics looks like this:

$$\begin{aligned} K_{sp} &= [Pb^{2+}][Cl^-]^2 \\ &= s \times (0.100)^2 \\ 1.7 \times 10^{-5} &= s \times 0.00100 \end{aligned}$$

therefore:

$$\begin{aligned} s &= \frac{1.7 \times 10^{-5}}{0.0100} \\ &= 1.7 \times 10^{-3}\,\text{M} \end{aligned} \tag{4.6.11}$$

Finally, compare that value with the simple saturated solution:

Original solution:

$$[Pb^{2+}] = 0.0162\ M \tag{4.6.12}$$

Solution in 0.100 M NaCl solution:

$$[Pb^{2+}] = 0.0017\ M \tag{4.6.13}$$

The concentration of the lead(II) ions has decreased by a factor of about 10. If more concentrated solutions of sodium chloride are used, the solubility decreases further.



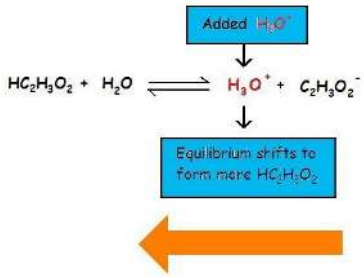
A Video Discussing Finding the Solubility of a Salt: Finding the Solubility of a Salt(opens in new window) [youtu.be]

Common Ion Effect with Weak Acids and Bases

Adding a common ion prevents the weak acid or weak base from ionizing as much as it would without the added common ion. The common ion effect suppresses the ionization of a weak acid by adding more of an ion that is a product of this equilibrium.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

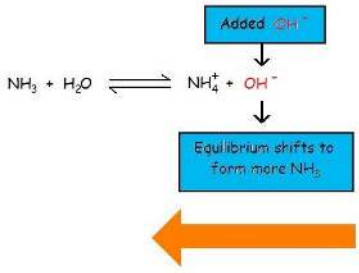
The common ion effect of H_3O^+ on the ionization of acetic acid



HC2H3O2 reactions with H2O to produce H3O plus and C2H3 O2 minus. If more H3O plus is added to the reaction, the equilibrium would shift to form more HC2H3O2.

When a strong acid supplies the common ion $\mathbf{H_3O^+}$ the equilibrium shifts to form more $\mathbf{HC_2H_3O_2}$.

The common ion effect suppresses the ionization of a weak base by adding more of an ion that is a product of this equilibrium. Now consider the common ion effect of $\mathbf{OH^-}$ on the ionization of ammonia



When a strong base supplies the common ion $\mathbf{OH^-}$ the equilibrium shifts to form more $\mathbf{NH_3}$.

NH3 reacts with H2 O to produce NH4 plus and OH minus. If more OH minus is added to the reaction, the equilibrium would shifts to form more NH3.

Adding the common ion of hydroxide shifts the reaction towards the left to decrease the stress (in accordance with Le Chatelier's Principle), forming more reactants. This decreases the reaction quotient, because the reaction is being pushed towards the left to reach equilibrium. The equilibrium constant, $K_b = 1.8 \times 10^{-5}$, does not change. The reaction is put out of balance, or equilibrium.

$$Q_a = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

At first, when more hydroxide is added, the quotient is greater than the equilibrium constant. The reaction then shifts right, causing the denominator to increase, decreasing the reaction quotient and pulling towards equilibrium and causing Q to decrease towards K.

Common Ion Effect on Solubility

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3\,Ca^{2+}(aq) + 2\,PO_4^{3-}(aq) \tag{4.6.14}$$

As you will discover in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate. The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[Ca^{2+}]^3[PO_4^{3-}]^2}{[Ca_3(PO_4)_2]} \tag{4.6.15}$$

$$[Ca_3(PO_4)_2]K = K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 \tag{4.6.16}$$

At 25°C and pH 7.00, K_{sp} for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts vary dramatically for different compounds (Table E3). Although K_{sp} is not a function of pH in Equation 4.6.15, changes in pH can affect the solubility of a compound.

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. **Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions.** This dependency is another example of the common ion effect where adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains

- $3 \times (1.14 \times 10^{-7}\ M) = 3.42 \times 10^{-7} M\ of\ Ca^{2+}$
- $2 \times (1.14 \times 10^{-7} M) = 2.28 \times 10^{-7} M\ of\ PO_4^{3-}$

according to the stoichiometry shown in Equation 4.6.15 (neglecting hydrolysis to form HPO_4^{2-}). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 4.6.15 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

Note

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

Example 4.6.5

Consider the reaction:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

What happens to the solubility of $PbCl_2$(s) when 0.1 M NaCl is added?

Solution

$$K_{sp} = 1.7 \times 10^{-5}$$

$$Q_{sp} = 1.8 \times 10^{-5}$$

Identify the common ion: Cl^-

Notice: $Q_{sp} > K_{sp}$ The addition of NaCl has caused the reaction to shift out of equilibrium because there are more dissociated ions. Typically, solving for the molarities requires the assumption that the solubility of $PbCl_2$ is equivalent to the concentration of Pb^{2+} produced because they are in a 1:1 ratio.

Because K_{sp} for the reaction is 1.7×10^{-5}, the overall reaction would be $(s)(2s)^2 = 1.7\times10^{-5}$. Solving the equation for s gives s= 1.62×10^{-2} M. The coefficient on Cl^- is 2, so it is assumed that twice as much Cl^- is produced as Pb^{2+}, hence the '2s.' The solubility equilibrium constant can be used to solve for the molarities of the ions at equilibrium.

The molarity of Cl^- added would be 0.1 M because Na^+ and Cl^- are in a 1:1 ration in the ionic salt, NaCl. Therefore, the overall molarity of Cl^- would be 2s + 0.1, with 2s referring to the contribution of the chloride ion from the dissociation of lead chloride.

$$Q_{sp} = [Pb^{2+}][Cl^-]^2 \quad (4.6.17)$$

$$1.8 \times 10^{-5} = (s)(2s + 0.1)^2 \quad (4.6.18)$$

$$s = [Pb^{2+}] \quad (4.6.19)$$

$$= 1.8 \times 10^{-3} M \quad (4.6.20)$$

$$2s = [Cl^-] \quad (4.6.21)$$

$$\approx 0.1M \quad (4.6.22)$$

Notice that the molarity of Pb^{2+} is lower when NaCl is added. The equilibrium constant remains the same because of the increased concentration of the chloride ion. To simplify the reaction, it can be assumed that $[Cl^-]$ is approximately 0.1M since the formation of the chloride ion from the dissociation of lead chloride is so small. The reaction quotient for $PbCl_2$ is greater than the equilibrium constant because of the added Cl^-. This therefore shift the reaction left towards equilibrium, causing precipitation and lowering the current solubility of the reaction. Overall, the solubility of the reaction decreases with the added sodium chloride.

Exercise 4.6.5

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



A Video Discussing the Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products (opens in new window) [youtu.be]

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Contributors and Attributions

- Emmellin Tung, Mahtab Danai (UCD)
- Jim Clark (ChemGuide)
- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

Learning Objectives

- To understand how adding a common ion affects the position of an acid–base equilibrium.
- To know how to use the Henderson-Hasselbalch approximation to calculate the pH of a buffer.

Buffers are solutions that maintain a relatively constant pH when an acid or a base is added. They therefore protect, or "buffer," other molecules in solution from the effects of the added acid or base. Buffers contain either a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+), and they are critically important for the proper functioning of biological systems. In fact, every biological fluid is buffered to maintain its physiological pH.

The Common Ion Effect: Weak Acids Combined with Conjugate Bases

To understand how buffers work, let's look first at how the ionization equilibrium of a weak acid is affected by adding either the conjugate base of the acid or a strong acid (a source of H^+). Le Chatelier's principle can be used to predict the effect on the equilibrium position of the solution. A typical buffer used in biochemistry laboratories contains acetic acid and a salt such as sodium acetate. The dissociation reaction of acetic acid is as follows:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \tag{4.6.23}$$

and the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3CO_2H]} \tag{4.6.24}$$

Sodium acetate (CH_3CO_2Na) is a strong electrolyte that ionizes completely in aqueous solution to produce Na^+ and $CH_3CO_2^-$ ions. If sodium acetate is added to a solution of acetic acid, Le Chatelier's principle predicts that the equilibrium in Equation 4.6.23 will shift to the left, consuming some of the added CH_3COO^- and some of the H^+ ions originally present in solution.

Because Na^+ is a **spectator ion**, it has no effect on the position of the equilibrium and can be ignored. The addition of sodium acetate produces a new equilibrium composition, in which $[H^+]$ is less than the initial value. Because $[H^+]$ has decreased, the pH will be higher. Thus adding a salt of the conjugate base to a solution of a weak acid increases the pH. This makes sense because sodium acetate is a base, and adding any base to a solution of a weak acid should increase the pH.

If we instead add a strong acid such as HCl to the system, $[H^+]$ increases. Once again the equilibrium is temporarily disturbed, but the excess H^+ ions react with the conjugate base ($CH_3CO_2^-$), whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3CO_2^-]$ than before. In both cases, only the equilibrium composition has changed; the ionization constant K_a for acetic acid remains the same. Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium, in this case $CH_3CO_2^-$, will therefore shift the equilibrium in the direction that reduces the concentration of the common ion. The shift in equilibrium is via the common ion effect.

> *Adding a common ion to a system at equilibrium affects the equilibrium composition, but not the ionization constant.*

Example 4.6.1

A 0.150 M solution of formic acid at 25°C (pKa = 3.75) has a pH of 2.28 and is 3.5% ionized.

a. Is there a change to the pH of the solution if enough solid sodium formate is added to make the final formate concentration 0.100 M (assume that the formic acid concentration does not change)?
b. What percentage of the formic acid is ionized if 0.200 M HCl is added to the system?

Given: solution concentration and pH, pK_a, and percent ionization of acid; final concentration of conjugate base or strong acid added

Asked for: pH and percent ionization of formic acid

Strategy:

A. Write a balanced equilibrium equation for the ionization equilibrium of formic acid. Tabulate the initial concentrations, the changes, and the final concentrations.
B. Substitute the expressions for the final concentrations into the expression for Ka. Calculate $[H^+]$ and the pH of the solution.
C. Construct a table of concentrations for the dissociation of formic acid. To determine the percent ionization, determine the anion concentration, divide it by the initial concentration of formic acid, and multiply the result by 100.

Solution:

A Because sodium formate is a strong electrolyte, it ionizes completely in solution to give formate and sodium ions. The Na^+ ions are spectator ions, so they can be ignored in the equilibrium equation. Because water is both a much weaker acid than formic acid and a much weaker base than formate, the acid–base properties of the solution are determined solely by the formic acid ionization equilibrium:

$$HCO_2H(aq) \rightleftharpoons HCO_2^-(aq) + H^+(aq)$$

The initial concentrations, the changes in concentration that occur as equilibrium is reached, and the final concentrations can be tabulated.

Final Concentration

ICE	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
Initial	0.150	1.00×10^{-7}	0.100
Change	−x	+x	+x
Equilibrium	(0.150 − x)	x	(0.100 + x)

B We substitute the expressions for the final concentrations into the equilibrium constant expression and make our usual simplifying assumptions, so

$$\begin{aligned} K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} &= \frac{(x)(0.100+x)}{0.150-x} \\ &\approx \frac{x(0.100)}{0.150} \\ &\approx 10^{-3.75} \\ &\approx 1.8 \times 10^{-4} \end{aligned}$$

Rearranging and solving for x,

$$\begin{aligned} x &= (1.8 \times 10^{-4}) \times \frac{0.150\ M}{0.100\ M} \\ &= 2.7 \times 10^{-4} \\ &= [H^+] \end{aligned}$$

The value of x is small compared with 0.150 or 0.100 M, so our assumption about the extent of ionization is justified. Moreover,

$$K_a C_{HA} = (1.8 \times 10^{-4})(0.150) = 2.7 \times 10^{-5}$$

which is greater than 1.0×10^{-6}, so again, our assumption is justified. The final pH is:

$$pH = -\log(2.7 \times 10^{-4}) = 3.57$$

compared with the initial value of 2.29. Thus adding a salt containing the conjugate base of the acid has increased the pH of the solution, as we expect based on Le Chatelier's principle; the stress on the system has been relieved by the consumption of H^+ ions, driving the equilibrium to the left.

C Because HCl is a strong acid, it ionizes completely, and chloride is a spectator ion that can be neglected. Thus the only relevant acid–base equilibrium is again the dissociation of formic acid, and initially the concentration of formate is zero. We can construct a table of initial concentrations, changes in concentration, and final concentrations.

$$HCO_2H(aq) \leftrightharpoons H^+(aq) + HCO_2^-(aq)$$

initial concentrations, changes in concentration, and final concentrations

	$[HCO_2H(aq)]$	$[H^+(aq)]$	$[HCO_2^-(aq)]$
initial	0.150	0.200	0
change	−x	+x	+x
final	(0.150 − x)	(0.200 + x)	x

To calculate the percentage of formic acid that is ionized under these conditions, we have to determine the final $[HCO_2^-]$. We substitute final concentrations into the equilibrium constant expression and make the usual simplifying assumptions, so

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{(0.200 + x)(x)}{0.150 - x} \approx \frac{x(0.200)}{0.150} = 1.80 \times 10^{-4}$$

Rearranging and solving for x,

$$x = (1.80 \times 10^{-4}) \times \frac{0.150\ M}{0.200\ M}$$
$$= 1.35 \times 10^{-4} = [HCO_2^-]$$

Once again, our simplifying assumptions are justified. The percent ionization of formic acid is as follows:

$$\text{percent ionization} = \frac{1.35 \times 10^{-4}\ M}{0.150\ M} \times 100\% = 0.0900\%$$

Adding the strong acid to the solution, as shown in the table, decreased the percent ionization of formic acid by a factor of approximately 38 (3.45%/0.0900%). Again, this is consistent with Le Chatelier's principle: adding H^+ ions drives the dissociation equilibrium to the left.

? Exercise 4.6.1

A 0.225 M solution of ethylamine ($CH_3CH_2NH_2$ with $pK_b = 3.19$) has a pH of 12.08 and a percent ionization of 5.4% at 20°C. Calculate the following:

a. the pH of the solution if enough solid ethylamine hydrochloride ($EtNH_3Cl$) is added to make the solution 0.100 M in $EtNH_3^+$
b. the percentage of ethylamine that is ionized if enough solid $NaOH$ is added to the original solution to give a final concentration of 0.050 M $NaOH$

Answer a

11.16

Answer b

1.3%



A Video Discussing the Common Ion Effect: The Common Ion Effecr(opens in new window) [youtu.be]

The Common Ion Effect: Weak Bases Combined with Conjugate Acids

Now let's suppose we have a buffer solution that contains equimolar concentrations of a weak base (B) and its conjugate acid (BH^+). The general equation for the ionization of a weak base is as follows:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \qquad (4.6.25)$$

If the equilibrium constant for the reaction as written in Equation 4.6.25 is small, for example $K_b = 10^{-5}$, then the equilibrium constant for the reverse reaction is very large: $K = \frac{1}{K_b} = 10^5$. Adding a strong base such as OH^- to the solution therefore causes the equilibrium in Equation 4.6.25 to shift to the left, consuming the added OH^-. As a result, the OH^- ion concentration in solution remains relatively constant, and the pH of the solution changes very little. Le Chatelier's principle predicts the same outcome: when the system is stressed by an increase in the OH^- ion concentration, the reaction will proceed to the left to counteract the stress.

If the pK_b of the base is 5.0, the pK_a of its conjugate acid is

$$pK_a = pK_w - pK_b = 14.0 - 5.0 = 9.0.$$

Thus the equilibrium constant for ionization of the conjugate acid is even smaller than that for ionization of the base. The ionization reaction for the conjugate acid of a weak base is written as follows:

$$BH^+(aq) + H_2O(l) \leftrightharpoons B(aq) + H_3O^+(aq) \tag{4.6.26}$$

Again, the equilibrium constant for the reverse of this reaction is very large: $K = 1/K_a = 10^9$. If a strong acid is added, it is neutralized by reaction with the base as the reaction in Equation 4.6.26 shifts to the left. As a result, the H^+ ion concentration does not increase very much, and the pH changes only slightly. In effect, a buffer solution behaves somewhat like a sponge that can absorb H^+ and OH^- ions, thereby preventing large changes in pH when appreciable amounts of strong acid or base are added to a solution.

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution. The more concentrated the buffer solution, the greater its buffer capacity. As illustrated in Figure 4.6.1, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

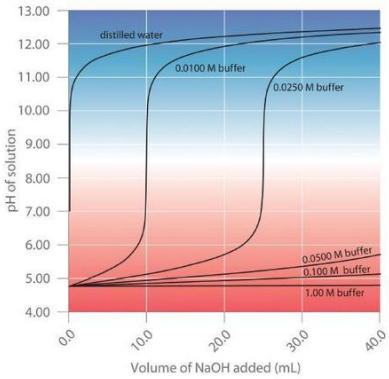


Figure 4.6.1: Effect of Buffer Concentration on the Capacity of a Buffer. (CC BY-SA-NC; Anonymous by request)
Graph of pH of solution against volume of NaOH added. Six different buffer concentrations are plotted.

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Calculating the pH of a Buffer

The pH of a buffer can be calculated from the concentrations of the weak acid and the weak base used to prepare it, the concentration of the conjugate base and conjugate acid, and the pK_a or pK_b of the weak acid or weak base. The procedure is analogous to that used in Example 4.6.1 to calculate the pH of a solution containing known concentrations of formic acid and formate.

An alternative method frequently used to calculate the pH of a buffer solution is based on a rearrangement of the equilibrium equation for the dissociation of a weak acid. The simplified ionization reaction is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{4.6.27}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{4.6.28}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{4.6.29}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{4.6.30}$$

Replacing the negative logarithms in Equation 4.6.30,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{4.6.31}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{4.6.32}$$

Equation 4.6.31 and Equation 4.6.32 are both forms of the Henderson-Hasselbalch approximation, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values.

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1$$

  in Equation 4.6.32. Because $\log 1 = 0$,

  $$pH = pK_a$$

  regardless of the actual concentrations of the acid and base. Recall that this corresponds to the midpoint in the titration of a weak acid or a weak base.
- $[base]/[acid] = 10$: In Equation 4.6.32, because $\log 10 = 1$,

  $$pH = pK_a + 1.$$
- $[base]/[acid] = 100$: In Equation 4.6.32, because $\log 100 = 2$,

  $$pH = pK_a + 2.$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = $pK_a - 1$. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> If [base] = [acid] for a buffer, then pH = pK_a. Changing this ratio by a factor of 10 either way changes the pH by ±1 unit.

Example 4.6.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)
b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equations 4.6.31 or 4.6.32) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 4.6.31), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]).$$

A

Inserting the given values into the equation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the [A^-]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 4.6.32, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\,M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall from Equation 16.23 that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w.$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \\ &= 5.23 + \log\left(\frac{0.119}{0.234}\right) \\ &= 5.23 - 0.294 \\ &= 4.94 \end{aligned}$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise 4.6.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68



A Video Discussing Using the Henderson Hasselbalch Equation: Using the Henderson Hasselbalch Equation(opens in new window) [youtu.be] (opens in new window)

The Henderson-Hasselbalch approximation ((Equation 4.6.31) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 4.6.3.

Example 4.6.3

The buffer solution in Example 4.6.2 contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution using the procedure from Example 4.6.1. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 4.6.32) to obtain the pH.

Solution:

The added HCl (a strong acid) or $NaOH$ (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

$$100\ \cancel{mL}\left(\frac{0.135\ mmol\ HCO_2H}{\cancel{mL}}\right) = 13.5\ mmol\ HCO_2H$$

$$100\ \cancel{mL}\left(\frac{0.215\ mmol\ HCO_2^-}{\cancel{mL}}\right) = 21.5\ mmol\ HCO_2^-$$

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

$$5.00\ \cancel{mL}\left(\frac{1.00\ mmol\ H^+}{\cancel{mL}}\right) = 5\ mmol\ H^+$$

B Next, we construct a table of initial amounts, changes in amounts, and final amounts:

$$HCO^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_2H(aq)$$

initial amounts, changes in amounts, and final amounts:

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 4.6.1 or the Henderson–Hasselbach approximation. Because we have performed many equilibrium calculations in this chapter, we'll take the latter approach. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation (Equation 4.6.32):

$$\begin{aligned} pH &= pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) \\ &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \end{aligned}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) \\ &= 3.75 - 0.050 = 3.70 \end{aligned}$$

Once again, this result makes sense on two levels. First, the addition of HCl has decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and $pK_a - 1$.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct a table of initial amounts, changes in amounts, and final amounts.

$$\mathrm{HCO_2H\,(aq) + OH^-\,(aq) \rightleftharpoons HCO_2^-\,(aq) + H_2O\,(l)}$$

initial amounts, changes in amounts, and final amounts

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Final	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$\begin{aligned} pH &= pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \\ &= 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) \\ &= 3.75 + 0.494 = 4.24 \end{aligned}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

? Exercise 4.6.3

The buffer solution from Example **4.6.2** contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M **NaOH** are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M **HCl** are added?

Answer a

5.30

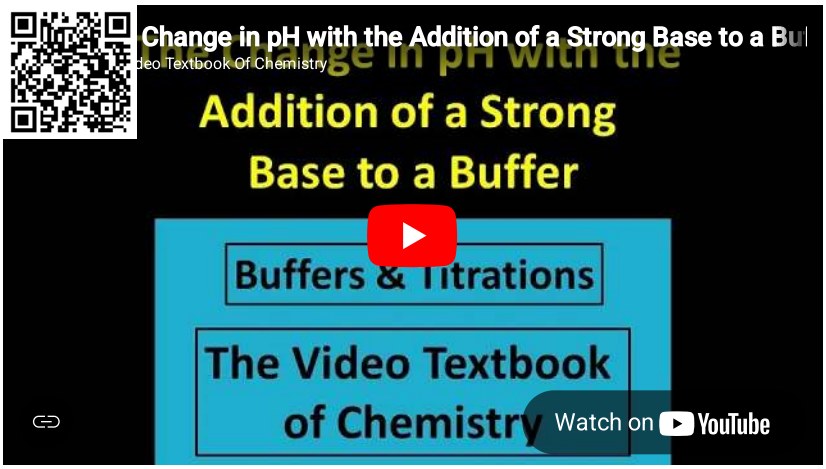
Answer b

4.42

Only the amounts (in moles or millimoles) of the acidic and basic components of the buffer are needed to use the Henderson-Hasselbalch approximation, not their concentrations.



A Video Discussing the Change in pH with the Addition of a Strong Acid to a Buffer: The Change in pH with the Addition of a Strong Acid to a Buffer(opens in new window) [youtu.be]



The Change in pH with the Addition of a Strong Base to a Buffer:

The Change in pH with the Addition of a Strong Base to a Buffer (opens in new window) [youtu.be]

The results obtained in Example **4.6.3** and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

> *The most effective buffers contain **equal** concentrations of an acid and its conjugate base.*

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure **4.6.2** for an acetic acid/sodium acetate buffer. Adding a given amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

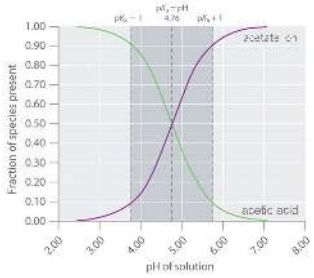


Figure **4.6.2**: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$). (CC BY-SA-NC; Anonymous by request)

Graph of mole fraction against pH of solution. The green line is acetic acid and the purple line is the acetate ion.



A Video Discussing The Buffer Region: The Buffer Region (opens in new window) [youtu.be]

The Relationship between Titrations and Buffers

There is a strong correlation between the effectiveness of a buffer solution and the titration curves discussed in Section 16.5. Consider the schematic titration curve of a weak acid with a strong base shown in Figure **4.6.3**. As indicated by the labels, the region around pK_a corresponds to the midpoint of the titration, when approximately half the weak acid has been neutralized. This portion of the titration curve corresponds to a buffer: it exhibits the smallest change in pH per increment of added strong base, as shown by the nearly horizontal nature of the curve in this region. The nearly flat

portion of the curve extends only from approximately a pH value of 1 unit less than the pK_a to approximately a pH value of 1 unit greater than the pK_a, which is why buffer solutions usually have a pH that is within ±1 pH units of the pK_a of the acid component of the buffer.

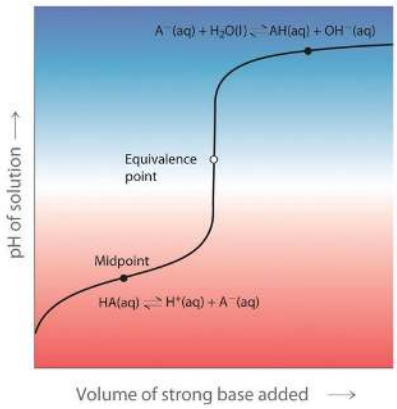


Figure **4.6.3**: The Relationship between Titration Curves and Buffers. (CC BY-SA-NC; Anonymous by request)

Titration curves graph pH of solution against volume of strong base added. On the curve we look for the midpoints and equivalence points.

This schematic plot of pH for the titration of a weak acid with a strong base shows the nearly flat region of the titration curve around the midpoint, which corresponds to the formation of a buffer. At the lower left, the pH of the solution is determined by the equilibrium for dissociation of the weak acid; at the upper right, the pH is determined by the equilibrium for reaction of the conjugate base with water.

In the region of the titration curve at the lower left, before the midpoint, the acid–base properties of the solution are dominated by the equilibrium for dissociation of the weak acid, corresponding to K_a. In the region of the titration curve at the upper right, after the midpoint, the acid–base properties of the solution are dominated by the equilibrium for reaction of the conjugate base of the weak acid with water, corresponding to K_b. However, we can calculate either K_a or K_b from the other because they are related by K_w.

Blood: A Most Important Buffer

Metabolic processes produce large amounts of acids and bases, yet organisms are able to maintain an almost constant internal pH because their fluids contain buffers. This is not to say that the pH is uniform throughout all cells and tissues of a mammal. The internal pH of a red blood cell is about 7.2, but the pH of most other kinds of cells is lower, around 7.0. Even within a single cell, different compartments can have very different pH values. For example, one intracellular compartment in white blood cells has a pH of around 5.0.

Because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

The acid–base equilibrium in the CO_2/HCO_3^- buffer system is usually written as follows:

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{4.6.33}$$

with $K_a = 4.5 \times 10^{-7}$ and $pK_a = 6.35$ at 25°C. In fact, Equation 4.6.33 is a grossly oversimplified version of the CO_2/HCO_3^- system because a solution of CO_2 in water contains only rather small amounts of H_2CO_3. Thus Equation 4.6.33 does not allow us to understand how blood is actually buffered, particularly at a physiological temperature of 37°C.

As shown in Equation 4.6.34, CO_2 is in equilibrium with H_2CO_3, but the equilibrium lies far to the left, with an H_2CO_3/CO_2 ratio less than 0.01 under most conditions:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{4.6.34}$$

with $K' = 4.0 \times 10^{-8}$ at 37°C. The true pK_a of carbonic acid at 37°C is therefore 3.70, not 6.35, corresponding to a K_a of 2.0×10^{-4}, which makes it a much stronger acid than Equation 4.6.33 suggests. Adding Equation 4.6.33 and Equation 4.6.34 and canceling H_2CO_3 from both sides give the following overall equation for the reaction of CO_2 with water to give a proton and the bicarbonate ion:

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \tag{4.6.35}$$

with $K' = 4.0 \times 10^{-3} (37°C)$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{4.6.36}$$

with $K_a = 2.0 \times 10^{-4} (37°C)$

$$CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \tag{4.6.37}$$

with $K = 8.0 \times 10^{-7} (37°C)$

The K value for the reaction in Equation 4.6.37 is the product of the true ionization constant for carbonic acid (K_a) and the equilibrium constant (K) for the reaction of $CO_2\,(aq)$ with water to give carbonic acid. The equilibrium equation for the reaction of CO_2 with water to give bicarbonate and a proton is therefore

$$K = \frac{[H^+][HCO_3^-]}{[CO_2]} = 8.0 \times 10^{-7} \tag{4.6.38}$$

The presence of a gas in the equilibrium constant expression for a buffer is unusual. According to Henry's law,

$$[CO_2] = kP_{CO_2}$$

where k is the Henry's law constant for CO_2, which is $3.0 \times 10^{-5}\ M/mmHg$ at 37°C. Substituting this expression for $[CO_2]$ in Equation 4.6.38,

$$K = \frac{[H^+][HCO_3^-]}{(3.0 \times 10^{-5}\ M/mmHg)(P_{CO_2})}$$

where P_{CO_2} is in mmHg. Taking the negative logarithm of both sides and rearranging,

$$pH = 6.10 + \log\left(\frac{[HCO_3^-]}{(3.0 \times 10^{-5} M/mm\ Hg)\ (P_{CO_2})}\right) \tag{4.6.39}$$

Thus the pH of the solution depends on both the CO_2 pressure over the solution and $[HCO_3^-]$. Figure 4.6.4 plots the relationship between pH and $[HCO_3^-]$ under physiological conditions for several different values of P_{CO_2}, with normal pH and $[HCO_3^-]$ values indicated by the dashed lines.

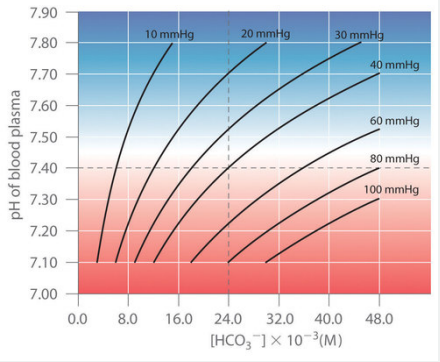


Figure **4.6.4**: Buffering in Blood: pH versus $[HCO_3^-]$ Curves for Buffers with Different Values of P_{CO_2}. Only those combinations of pH and $[HCO_3^-]$ that lie on a given line are allowed for the particular value of P_{CO_2} indicated. Normal values of blood plasma pH and $[HCO_3^-]$ are indicated by dashed lines. (CC BY-SA-NC; Anonymous by request)

According to Equation 4.6.39, adding a strong acid to the CO_2/HCO_3^- system causes $[HCO_3^-]$ to decrease as HCO_3^- is converted to CO_2. Excess CO_2 is released in the lungs and exhaled into the atmosphere, however, so there is essentially no change in P_{CO_2}. Because the change in $[HCO_3^-]/P_{CO_2}$ is small, Equation 4.6.39 predicts that the change in pH will also be rather small. Conversely, if a strong base is added, the OH^- reacts with CO_2 to form HCO_3^-, but CO_2 is replenished by the body, again limiting the change in both $[HCO_3^-]/P_{CO_2}$ and pH. The CO_2/HCO_3^- buffer system is an example of an open system, in which the total concentration of the components of the buffer change to keep the pH at a nearly constant value.

If a passenger steps out of an airplane in Denver, Colorado, for example, the lower P_{CO_2} at higher elevations (typically 31 mmHg at an elevation of 2000 m versus 40 mmHg at sea level) causes a shift to a new pH and $[HCO_3^-]$. The increase in pH and decrease in $[HCO_3^-]$ in response to the decrease in P_{CO_2} are responsible for the general malaise that many people experience at high altitudes. If their blood pH does not adjust rapidly, the condition can develop into the life-threatening phenomenon known as altitude sickness.



A Video Summary of the pH Curve for a Strong Acid/Strong Base Titration:

Summary of the pH Curve for a Strong Acid/Strong Base Titration(opens in new window) [youtu.be]

Summary

Buffers are solutions that resist a change in pH after adding an acid or a base. Buffers contain a weak acid (HA) and its conjugate weak base (A^-). Adding a strong electrolyte that contains one ion in common with a reaction system that is at equilibrium shifts the equilibrium in such a way as to reduce the concentration of the common ion. The shift in equilibrium is called the common ion effect. Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends strongly on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer (the K_a or K_b), whereas its buffer capacity depends solely on the concentrations of the species in the solution. The pH of a buffer can be calculated using the Henderson-Hasselbalch approximation, which is valid for solutions whose concentrations are at least 100 times greater than their K_a values. Because no single buffer system can effectively maintain a constant pH value over the physiological range of approximately 5 to 7.4, biochemical systems use a set of buffers with overlapping ranges. The most important of these is the CO_2/HCO_3^- system, which dominates the buffering action of blood plasma.

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4.7: Use of solubility properties for Chemical Separation

Learning Objectives

- Calculate ion concentrations to maintain a heterogeneous equilibrium.
- Calculate pH required to precipitate a metal hydroxide.
- Design experiments to separate metal ions in a solution of mixtures of metals.

A mixture of metal ions in a solution can be separated by precipitation with anions such as Cl^-, Br^-, SO_4^{2-}, CO_3^{2-}, S^{2-}, $Cr_2O_4^{2-}$, PO_4^{2-}, OH^- etc. When a metal ion or a group of metal ions form insoluble salts with a particular anion, they can be separated from others by precipitation. We can also separate the anions by precipitating them with appropriate metal ions. There are no definite dividing lines between **insoluble salts, sparingly soluble**, and **soluble salts**, but concentrations of their saturated solutions are small, medium, and large. Solubility products are usually listed for insoluble and sparingly soluble salts, but they are not given for soluble salts. Solubility products for soluble salts are very large.

What type of salts are usually soluble, sparingly soluble and insoluble? The following are some general guidelines, but these are not precise laws.

- All nitrates are soluble. The singly charged large NO_3^- ions form salts with high solubilities. So do ClO_4^-, ClO_3^-, NO_2^-, $HCOO^-$, and CH_3COO^-.
- All chlorides, bromides, and iodides are soluble except those of Ag^+, Hg_2^{2+}, and Pb^{2+}. CaF_2, BaF_2, and PbF_2 are also insoluble.
- All sulfates are soluble, except those of Ba^{2+}, Sr^{2+}, and Pb^{2+}. The doubly charged sulfates are usually less soluble than halides and nitrates.
- Most singly charge cations K^+, Na^+, NH_4^+ form soluble salts. However, $K_3Co(NO_2)_6$ and $(NH_4)_3Co(NO_2)_6$ are insoluble.

These are handy rules for us to have if we deal with salts often. On the other hand, solubility is an important physical property of a substance, and these properties are listed in handbooks.

Chemical Separation of Metal Ions

Formation of crystals from a saturated solution is a **heterogeneous equilibrium** phenomenon, and it can be applied to separate various chemicals or ions in a solution. When solubilities of two metal salts are very different, they can be separated by precipitation. The K_{sp} values for various salts are valuable information, and some data are given in Table E3. In the first two examples, we show how barium and strontium can be separated as chromate.

Example 4.7.1

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. What concentration of potassium chromate will precipitate the maximum amount of either the barium or the strontium chromate from an equimolar 0.30 M solution of barium and strontium ions without precipitating the other?

Solution

Since the K_{sp} for barium chromate is smaller, we know that $BaCrO_4$ will form a precipitate first as $[CrO_4^{2-}]$ increases so that Q_{sp} for $BaCrO_4$ also increases from zero to K_{sp} of $BaCrO_4$, at which point, $BaCrO_4$ precipitates. As $[CrO_4^{2-}]$ increases, $[Ba^{2+}]$ decreases. Further increase of $[CrO_4^{2-}]$ till Q_{sp} for $SrCrO_4$ increases to K_{sp} of $SrCrO_4$; it then precipitates.

Let us write the equilibrium equations and data down to help us think. Let x be the concentration of chromate to precipitate Sr^{2+}, and y be that to precipitate Ba^{2+}:

$$SrCrO_4(s) \rightarrow Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

According to the definition of K_{sp} we have we have $K_{sp} = (0.30)(x) = 3.6 \times 10^{-5}$. Solving for x gives

$$x = \frac{3.6 \times 10^{-5}}{0.30} = 1.2 \times 10^{-4} M$$

Further, let y be the concentration of chromate to precipitate precipitate Ba^{2+}:

$$BaCrO_4(s) \rightarrow Ba^{2+}(aq) + CrO_4{}^{2-}(aq)$$

with $K_{sp} = (0.30)(y) = 1.2 \times 10^{-10}$. Solving for y gives

$$y = \frac{1.2 \times 10^{-10}}{0.30} = 4.0 \times 10^{-10}\ M$$

The K_{sp}'s for the two salts indicate $BaCrO_4$ to be much less soluble, and it will precipitate before any $SrCrO_4$ precipitates. If chromate concentration is maintained less than $1.2 \times 10^{-4} M$, then all Sr^{2+} ions will remain in the solution.

Discussion

In reality, controling the increase of $[CrO_4{}^{2-}]$ is very difficult.

Example 4.7.2

The K_{sp} for strontium chromate is 3.6×10^{-5} and the K_{sp} for barium chromate is 1.2×10^{-10}. Potassium chromate is added a small amount at a time to first precipitate $BaCrO_4$. Calculate $[Ba^{2+}]$ when the first trace of $SrCrO_4$ precipitate starts to form in a solution that contains 0.30 M each of Ba^{2+} and Sr^{2+} ions.

Solution

From the solution given in Example 4.7.1, $[CrO_4{}^{2-}] = 3.6 \times 10^{-4}\ M$ when $SrCrO_4$ starts to form. At this concentration, the $[Ba^{2+}]$ is estimated at $3.6 \times 10^{-4} = 1.2 \times 10^{-10}$.

The K_{sp} of $BaCrO_4$.

Thus,

$$[Ba^{2+}] = 3.33 \times 10^{-7}\ M$$

Very small indeed, compared to 0.30. In the fresh precipitate of $SrCrO_4$, the molar ratio of $SrCrO_4$ to $BaCrO_4$ is

$$\frac{0.30}{3.33 \times 10^{-7}} = 9.0 \times 10^{5}.$$

Hence, the amount of Ba^{2+} ion in the solid is only 1×10^{-6} (i.e., 1 ppm) of all metal ions, providing that all the solid was removed when

$$[CrO_4{}^{2-}] = 3.6 \times 10^{-4} M.$$

Discussion

The calculation shown here indicates that the separation of Sr and Ba is pretty good. In practice, an impurity level of 1 ppm is a very small value.

Example 4.7.3

What reagent should you use to separate silver and lead ions that are present in a solution? What data or information will be required for this task?

Solution

The K_{sp}'s for salts of silver and lead are required. We list the K_{sp}'s for chlorides and sulfates in a table here. These value are found in the Handbook Menu of our website as Salts K_{sp}.

Solutions to Example 17.6.3

Because the K_{sp}'s $AgCl$ and $PbCl_2$ are very different, chloride, Cl^-, apppears a good choice of negative ions for their separation.

The literature also indicates that $PbCl_2$ is rather soluble in warm water, and by heating the solution to 350 K (80°C), you can keep Pb^{2+} ions in solution and precipitate $AgCl$ as a solid. The solubility of $AgCl$ is very small even at high temperatures.

Discussion

Find more detailed information about the solubility of lead chloride as a function of temperature.

Salt	K_{sp}	Salt	K_{sp}
$AgCl$	1.8×10^{-10}	Ag_2SO_4	1.4×10^{-5}
Hg_2Cl_2	1.3×10^{-18}	$BaSO_4$	1.1×10^{-10}
$PbCl_2$	1.7×10^{-5}	$CaSO_4$	2.4×10^{-5}
		$PbSO_4$	6.3×10^{-7}
		$SrSO_4$	3.2×10^{-7}

Can sulfate be used to separate silver and lead ions? Which one will form a precipitate first as the sulfate ion concentration increases? What is the $[Pb^{2+}]$ when Ag_2SO_4 begins to precipitate in a solution that contains 0.10 M Ag^+?



The Separation of Two Ions by a Difference in Solubility: The Separation of Two Ions by a Difference in Solubility(opens in new window) [youtu.be]

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4.8: Complex Ion Equilibria

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure 4.8.1. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.



Figure 4.8.1: The Formation of Complex Ions. An aqueous solution of $\mathbf{CuSO_4}$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$\mathbf{Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1} \tag{4.8.1}$$

$$\mathbf{[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2} \tag{4.8.2}$$

$$\mathbf{[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3} \tag{4.8.3}$$

$$\mathbf{[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4} \tag{4.8.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four $\mathbf{NH_3}$ ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{4.8.5}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**. The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{4.8.6}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table **4.8.1**.

Table **4.8.1**: Common Complex Ions

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from Lange's Handbook of Chemistry, 15th ed. (1999).

Example 4.8.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 4.8.5 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 4.8.6) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 4.8.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous

ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65 \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M \tag{4.8.7}$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define x as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is $-x$, and the change in the concentration of ammonia is $+4x$, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	$+x$	$+4x$	$-x$
final	x	0.66 + 4x	0.0846 − x

B Substituting the final concentrations into the expression for the formation constant (Equation 4.8.6) and assuming that x << 0.0846, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13}$$
$$x = 2.1 \times 10^{-14}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 4.8.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer

2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To

fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

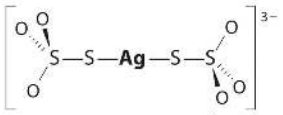
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)} \tag{4.8.8}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°C \tag{4.8.9}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^{+}_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{4.8.10}$$

with

$$K_f = 2.9 \times 10^{13} \tag{4.8.11}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad K_{sp} = 5.35 \times 10^{-13} \tag{4.8.12}$$

$$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) \quad K_f = 2.9 \times 10^{13} \tag{4.8.13}$$

$$AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq) \quad K = K_{sp}K_f = 15 \tag{4.8.14}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 4.8.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium [Ag+] = $[Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77 \times 10^{-10}$$

$$x = 1.33 \times 10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77 \times 10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = 1.77 \times 10^{-10} \tag{4.8.15}$$

$$Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^- \quad K_f = 1.1 \times 10^5 \tag{4.8.16}$$

$$AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^- \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{4.8.17}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[AgCl_2^-]}{[Cl^-]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 4.8.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$$K_{sp} = 2.9 \times 10^{-29} \text{ for } HgI_2 \text{ and } K_f = 6.8 \times 10^{29} \text{ for } [HgI_4]^{2-}.$$

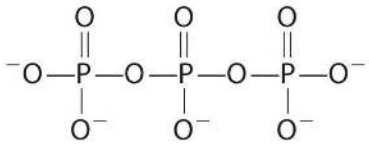
Answer a

1.9×10^{-10} M

Answer a

1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



triphosphate

$$Ca^{2+}(aq) + O_3POPO_4^{4-}(aq) \rightleftharpoons [Ca(O_3POPO_3)]^{2-}(aq) \tag{4.8.18}$$

with

$$K_f = 4 \times 10^4 \tag{4.8.19}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

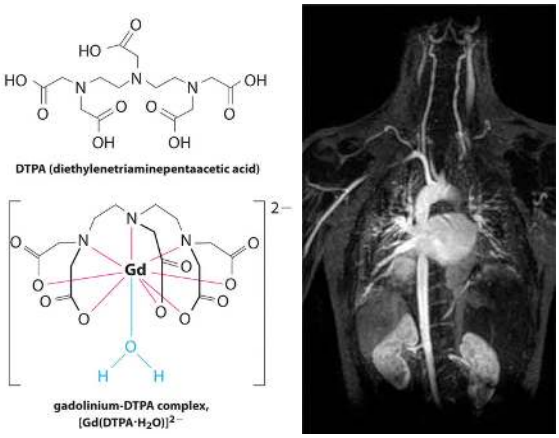


Figure 4.8.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this

problem, scientists have developed a class of metal complexes known as “MRI contrast agents.” Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to “see” each of these separately (Figure **4.8.2**). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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4.E: Aqueous Ionic Equilibrium (More Practice Problems)

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4.E: Buffer, Solubility, Common Ion Effects, and Acid-Base Titration (Practice Problems with Answers)

17.1: The Common-Ion Effect

17.2: Buffered Solutions

Conceptual Problems

1. Explain why buffers are crucial for the proper functioning of biological systems.

2. What is the role of a buffer in chemistry and biology? Is it correct to say that buffers prevent a change in $[H_3O^+]$? Explain your reasoning.

3. Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.

4. Which region of the titration curve of a weak acid or a weak base corresponds to the region of the smallest change in pH per amount of added strong acid or strong base?

5. If you were given a solution of sodium acetate, describe two ways you could convert the solution to a buffer.

6. Why are buffers usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base?

7. The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?

a. a buffer
b. a solution of a salt of a weak base
c. a solution of a weak acid
d. diluting a strong base

8. Which of the following will produce a buffer solution? Explain your reasoning in each case.

a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
c. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl
d. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M $NaOH$
e. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M $NaOH$.

9. Which of the following will produce a buffer solution? Explain your reasoning in each case.

a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium acetate
c. mixing 100 mL of 0.1 M acetic acid and 100 mL of 0.1 M $NaOH$
d. mixing 100 mL of 0.1 M acetic acid and 50 mL of 0.1 M $NaOH$
e. mixing 100 mL of 0.1 M sodium acetate and 50 mL of 0.1 M acetic acid

10. Use the definition of Kb for a weak base to derive the following expression, which is analogous to the Henderson-Hasselbalch approximation but for a weak base (B) rather than a weak acid (HA):

$$pOH = pK_b - \log\left(\frac{[base]}{[acid]}\right) \tag{4.E.1}$$

11. Why do biological systems use overlapping buffer systems to maintain a constant pH?

12. The CO_2/HCO_3^- buffer system of blood has an effective pK_a of approximately 6.1, yet the normal pH of blood is 7.4. Why is CO_2/HCO_3^- an effective buffer when the pK_a is more than 1 unit below the pH of blood? What happens to the pH of blood when the CO_2 pressure increases? when the O_2 pressure increases?

13. Carbon dioxide produced during respiration is converted to carbonic acid (H_2CO_3). The pK_a1 of carbonic acid is 6.35, and its pK_a2 is 10.33. Write the equations corresponding to each pK value and predict the equilibrium position for each reaction.

Answer

1. Buffers are crucial for the proper function of biological systems because they help maintain a relatively constant pH that maintains homeostasis and this is required for bodily function. For example, buffers can prevent stomach acid from being too acidic in which tissues and other parts of the body would be harmed.

2. The role of a buffer in chemistry and biology is to resist pH changes upon the addition of an acid or base. It is correct to say that buffers prevent a change in hydronium ion concentration because the pH is a measure of the acidity or alkalinity of a solution.

3. The most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base because when placed in the Henderson-Hasselbalch equation the pH approximately equals the pK_a. This is the goal because the more the ratio needs to differ to achieve the desired pH, the less effective the buffer and it should not differ by more than tenfold.

4. The region after the equivalence point on a titration curve of a weak acid or a weak base corresponds to the smallest change in pH per amount of added strong acid or strong base. This is because the strong acid or strong base completely neutralized the weak acid or weak base in which the pH remains constant relative to the strong acid or strong base.

5. Sodium acetate is a salt, therefore it can't be regarded as an acid or a base. One way to convert the solution to a buffer is to combine sodium acetate with a weak acid such as acetic acid. The sodium acetate would react with the hydronium ions and the acetic acid would react with hydroxide ions to prevent drastic changes in pH. Another way to convert the solution to a buffer is by titrating a weak acid and strong base or strong base and weak acid. For example, combining acetic acid to sodium hydroxide to produce sodium acetate (a neutralization reaction).

6.

Buffers are usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base because the ability of a buffer solution to maintain a nearly constant pH due to a small amount of acid or base is greatest at the pK_a and decreases as the pH of the solution goes above or below the pK_a.

$pH = pK_a + log(\frac{[B]}{[A]})$

When $\frac{[B]}{[A]} = 10$: $pH = pK_a + 1$

When $\frac{[B]}{[A]} = \frac{1}{10}$: $pH = pK_a - 1$

7.

a. I would use the region around the midpoint of the titration to describe the behavior of a buffer because the midpoint of the titration is defined as the point at which exactly enough acid or base has been added to neutralize one-half of the acid or the base originally present while maintaining a relatively constant pH.

b. I would use the equivalence point region to describe the behavior of a solution of a salt of a weak base because at this point the amount of titrant added is enough to completely neutralize the solution.

c. I would use the starting point region of the titration curve to describe the behavior of the solution of a weak acid because it is expected to be at a higher pH than a strong acid but lower than pH 7.

d. I would use the region after the equivalence point to describe the dilution of a strong base because in this region one can predict the pH by simply taking into account the amount of excess base.

8.

a. This will not produce a buffer solution because the hydrochloric acid completely neutralizes the sodium fluoride to give sodium chloride.

b. This will produce a buffer solution because the hydrochloric acid neutralizes only half of the acetic acid to give a solution containing equal amounts of hydrofluoric acid and sodium chloride.

c. This will not produce a buffer solution because hydrofluoric acid is a weak acid and hydrochloric acid is a strong acid.

d. This will produce a buffer solution because the solution will contain a 2:1 ratio of hydrofluoric acid and sodium hydroxide.

e. This will not produce a buffer solution solution because sodium fluoride is a weak base and sodium hydroxide is a strong base.

9.

a. This will not produce a buffer because the hydrochloric acid completely neutralizes the sodium acetate to give acetic acid and sodium chloride.

b. This will produce a buffer because the HCl neutralizes only half of the sodium acetate to give a solution containing equal amounts of acetic acid and sodium acetate.

c. This will not produce a buffer because the sodium hydroxide completely neutralizes the acetic acid to give sodium acetate.

d. This will produce a buffer because the sodium hydroxide neutralizes only half of the acetic acid to give a solution containing equal amounts of acetic acid and sodium acetate.

e. This will produce a buffer because the solution will contain a 2:1 ratio of sodium acetate and acetic acid.

10.

For pH:

$$HA \overset{K_a}{\rightleftharpoons} A^- + H^+$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$log(K_a) = log([H^+]) + log(\frac{[A^-]}{[HA]})$$

$$-pK_a = -pH + log(\frac{[A^-]}{[HA]})$$

$$pH = pK_a + log(\frac{[A^-]}{[HA]})$$

For pOH:

$$A^- \overset{K_b}{\rightleftharpoons} HA + OH^-$$

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$log(K_b) = log([OH^-]) + log(\frac{[HA]}{[A^-]})$$

$$-pK_b = -pOH - log(\frac{[A^-]}{[HA]})$$

$$pOH = pK_b - log(\frac{[A^-]}{[HA]})$$

Helpful Equations:

$$pK_a = -log(K_a) \rightarrow -pK_a = log(K_a)$$

$$-log([H^+]) = pH \rightarrow log([H^+]) = -pH$$

$$pK_b = -log(K_b) \rightarrow -pK_a = log(K_b)$$

$$-log([OH^-]) = pOH \rightarrow log([OH^-]) = -pOH$$

11. Biological systems use overlapping buffer systems to maintain a constant pH because no single buffer system can effectively maintain a constant pH value over the entire physiological range of approximately pH 5.0 to 7.4.

12. CO_2/HCO_3^- is an effective buffer when the pK_a is more than 1 unit below the pH of blood because the kidneys help control acid-base balance by excreting hydrogen ions and generating bicarbonate that helps maintain blood plasma pH within the normal range. The bicarbonate ion can combine with a proton to form carbonic acid and the more protons are absorbed from the solution the more the pH increases, resulting in hemoglobin absorbing oxygen. Carbonic acid, which can be formed from carbon dioxide and water, can dissociate into a proton and bicarbonate ion which increases the hydrogen ion concentration and lowers the blood pH, resulting in hemoglobin proteins releasing oxygen. The carbonic acid, which can be formed from bicarbonate, is converted to carbon dioxide and water via a very fast enzymatic reaction. Carbon dioxide, being volatile, can be rapidly expelled from the body at varying rates by respiration.

13.

$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \; pK_{a1} = 6.35$ left

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \; pK_{a2} = 10.33$ right

Numerical Problems

1.Benzenesulfonic acid ($pKa = 0.70$) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:

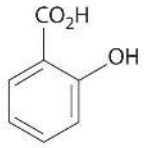
a. the pH of a 0.286 M solution of benzenesulfonic acid
b. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M

2. Phenol has a pK_a of 9.99. Calculate the following:

a. the pH of a 0.195 M solution
b. the percent increase in the concentration of phenol after adding enough solid sodium phenoxide (the sodium salt of the conjugate base) to give a total phenoxide concentration of 0.100 M

3. Salicylic acid is used in the synthesis of acetylsalicylic acid, or aspirin. One gram dissolves in 460 mL of water to create a saturated solution with a pH of 2.40.

a. What is the K_a of salicylic acid?
b. What is the final pH of a saturated solution that is also 0.238 M in sodium salicylate?
c. What is the final pH if 10.00 mL of 0.100 M HCl are added to 150.0 mL of the buffered solution?
d. What is the final pH if 10.00 mL of 0.100 M NaOH are added to 150.0 mL of the buffered solution?



salicylic acid

4. An intermediate used in the synthesis of perfumes is valeric acid, also called pentanoic acid. The pK_a of pentanoic acid is 4.84 at 25°C.

a. What is the pH of a 0.259 M solution of pentanoic acid?
b. Sodium pentanoate is added to make a buffered solution. What is the pH of the solution if it is 0.210 M in sodium pentanoate?
c. What is the final pH if 8.00 mL of 0.100 M HCl are added to 75.0 mL of the buffered solution?
d. What is the final pH if 8.00 mL of 0.100 M NaOH are added to 75.0 mL of the buffered solution?

Answer

1.

a. $pH = -log([H^+]) = -log(0.2388) = 0.62$

$$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-0.70} \times 0.286\,M} = 0.2388$$

b. $pH = -log([H^+]) = -log(0.14125) = 0.850$

$$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-0.70} \times 0.100\,M} = 0.14125$$

2.

a. $pH = -log(4.46 \times 10^{-6}) = 5.35$

$$K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]} = \frac{x^2}{0.195} \rightarrow 10^{-9.99} = \frac{x^2}{0.195} \rightarrow x = 4.46 \times 10^{-6}$$

$Assumption\ Valid: \frac{4.46\times10^{-6}}{0.195\ M} \times 100\% < 5\%$

	C_6H_5OH	H_2O	$C_6H_5O^-$	H_3O^+
I	0.195	-	0	0
C	-x	-	+x	+x
E	0.195-x	-	x	x

b. $Percent\ increase = \frac{3.20\times10^{-6}}{4.46\times10^{-6}} x100\% = 71.6\%$

$K_a = \frac{[C_6H_5O^-][H_3O^+]}{C_6H_5OH} = \frac{x^2}{0.100} \rightarrow 10^{-9.99} = \frac{x^2}{0.100} \rightarrow x = 3.20 \times 10^{-6}$

3.

a. $K_a = \frac{[C_9H_8O_4][H_3O^+]}{[C_7H_6O_3]} = \frac{x^2}{0.015739} \rightarrow \frac{(3.98\times10^{-3})^2}{0.015739} = 1.0 \times 10^{-3}$

$C_7H_6O_3 : 1\ g \times \frac{1\ mol}{138.121\ g\ mol} \times \frac{1}{460\ mL \times \frac{1\ L}{1000\ mL}} = 0.015739\ M$

$pH = -log([H^+]) \rightarrow [H^+] = 10^{-pH} = 10^{-2.40} = 3.98 \times 10^{-3}$

b. $pH = pK_a + log(\frac{[C_7H_5NaO_3]}{[C_7H_6O_3]}) = -log(1.01 \times 10^{-3}) + log(\frac{0.238}{0.015739}) = 4.17$

c. $pH = pK_a + log(\frac{mol\ C_7H_5NaO_3 - mol\ HCl}{mol\ C_9H_8O_4 + mol\ HCl}) = -log(1.01 \times 10^{-3}) + log(\frac{0.0357-0.001}{0.00236085+0.001}) = 4.01$

$HCl : .01\ L \times 0.100\ M = 0.001\ mol$

$C_7H_5NaO_3 : 0.15\ L \times 0.238\ M = 0.0357\ mol$

$C_7H_6O_3 : 0.15\ L \times 0.015739\ M = 0.00236085\ mol$

d. $pH = pK_a + log(\frac{mol\ C_7H_5NaO_3 + mol\ NaOH}{mol\ C_9H_8O_4 - mol\ NaOH}) = -log(1.01 \times 10^{-3}) + log(\frac{0.0357+0.001}{0.00236085-0.001}) = 4.43$

$NaOH : .01\ L \times 0.100\ M = 0.001\ mol$

$C_7H_5NaO_3 : 0.15\ L \times 0.238\ M = 0.0357\ mol$

$C_7H_6O_3 : 0.15\ L \times 0.015739\ M = 0.00236085\ mol$

4.

a. $pH = -log([H^+]) = -log(3.7 \times 10^{-6}) = 5.43$

$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-4.84} \times 0.259\ M} = 3.7 \times 10^{-6}$

b. $pH = pK_a + log(\frac{B}{A}) = 4.84 + log(\frac{0.210}{0.259}) = 4.75$

c. $pH = pK_a + log(\frac{B}{A}) = 4.84 + log(\frac{mol\ C_5H_9NaO_2 - mol\ HCl}{mol\ C_5H_{10}O_2 + mol\ HCl}) = 4.84 + log(\frac{0.01575-8\times10^{-4}}{0.019425+8\times10^{-4}}) = 4.71$

$HCl : 8.00\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.100\ M = 8 \times 10^{-4}\ mol$

$C_5H_9NaO_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.210\ M = 0.01575\ mol$

$C_5H_{10}O_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.259\ M = 0.019425\ mol$

d. $pH = pK_a + log(\frac{B}{A}) = 4.84 + log(\frac{mol\ C_5H_9NaO_2 + mol\ NaOH}{mol\ C_5H_{10}O_2 - mol\ NaOH}) = 4.84 + log(\frac{0.01575+8\times10^{-4}}{0.019425-8\times10^{-4}}) = 6.07$

$NaOH : 8.00\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.100\ M = 8 \times 10^{-4}\ mol$

$C_5H_9NaO_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.210\ M = 0.01575\ mol$

$C_5H_{10}O_2 : 75.0\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.259\ M = 0.019425\ mol$

17.3: Acid-Base Titrations

Conceptual Problems

1. Why is the portion of the titration curve that lies below the equivalence point of a solution of a weak acid displaced upward relative to the titration curve of a strong acid? How are the slopes of the curves different at the equivalence point? Why?

2. Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.

a. An aqueous solution of $NaOH$ is titrated with 0.100 M HCl.
b. An aqueous solution of ethylamine ($CH_3CH_2NH_2$) is titrated with 0.150 M HNO_3
c. An aqueous solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is titrated with 0.050 M KOH.

3. The pKa values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?

a. titrating a solution of $Ba(OH)_2$ with 0.100 M HCl
b. titrating a solution of trimethylamine (Me_3N) with 0.150 M HNO_3
c. titrating a solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) with 0.050 M KOH

4. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not usually the case in titrations of weak acids or weak bases?

5. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?

6. Describe what is occurring on a molecular level during the titration of a weak acid, such as acetic acid, with a strong base, such as $NaOH$, at the following points along the titration curve. Which of these points corresponds to $pH = pK_a$?

a. at the beginning of the titration
b. at the midpoint of the titration
c. at the equivalence point
d. when excess titrant has been added

7. On a molecular level, describe what is happening during the titration of a weak base, such as ammonia, with a strong acid, such as HCl, at the following points along the titration curve. Which of these points corresponds to $pOH = pK_b$?

a. at the beginning of the titration
b. at the midpoint of the titration
c. at the equivalence point
d. when excess titrant has been added

8. For the titration of a weak acid with a strong base, use the K_a expression to show that $pH = pK_a$ at the midpoint of the titration.

9. Chemical indicators can be used to monitor pH rapidly and inexpensively. Nevertheless, electronic methods are generally preferred. Why?

10. Why does adding ammonium chloride to a solution of ammonia in water decrease the pH of the solution?

11. Given the equilibrium system $CH_3CO_2H\ (aq) \rightleftharpoons CH_3CO_2^-\ (aq) + H^+\ (aq)$, explain what happens to the position of the equilibrium and the pH in each case.

a. Dilute HCl is added.
b. Dilute $NaOH$ is added.
c. Solid sodium acetate is added.

12. Given the equilibrium system $CH_3NH_2\,(aq) + H_2O\,(l) \rightleftharpoons CH_3NH_3^+\,(aq) + OH^-\,(aq)$, explain what happens to the position of the equilibrium and the pH in each case.

a. Dilute HCl is added.
b. Dilute $NaOH$ is added.
c. Solid $CH_3NH_3^+Cl^-$ is added.

Answers

1. The portion of the titration curve that lies below the equivalence point of a solution of a weak acid is displaced upward relative to the titration curve of a strong acid because the starting point of a weak acid is at a higher pH compared to that of a strong acid. The slope for a strong acid is greater compared to that of a weak acid because when a weak acid is neutralized, the solution that remains is basic because the acid's conjugate base remains in solution.

2.

a. The solution will be neutral at the equivalence point because sodium hydroxide is a strong base and hydrochloric acid is a strong acid.

b. The solution will be acidic at the equivalence point because ethylamine is a weak base and nitric acid is a strong acid.

c. The solution will be basic at the equivalence point because aniline hydrochloride is a weak acid and potassium hydroxide is a strong base.

3.

a. Barium hydroxide is a strong base and hydrochloric acid is a strong acid thus phenol red with the $pK_a = 7.4$ is best suited for the reaction.

b. Trimethylamine is a weak base and nitric acid is a strong acid thus bromophenol blue with the $pK_a = 4.1$ is best suited for the reaction.

c. Aniline hydrochloride is a weak acid and potassium hydroxide is a strong base thus phenolphthalein with $pK_a = 9.5$ is best suited for the reaction.

4. This is not usually the case in the titration of weak acids and weak bases because weak acids and weak bases would only ionize partially, thus complete neutralization does not occur.

5. The titration curve for a strong acid with a strong base is identical in shape above the equivalence point of the titration curve with a weak acid and strong base because both cases involve the addition of strong base. Not only does the strong base completely neutralize the acid but there is an excess of a strong base that makes the solution basic.

6.

a. The titration begins with a pH is higher than the titration of a strong acid. At the beginning of the titration, there is a sharp increase in pH because the anion of the weak acid becomes a common ion that reduces the ionization of the acid.

b. There is a sharp increase at the beginning of the titration that changes gradually due to the solution becoming a buffer. This continues until the strong base has overcome the buffer capacity. At the midpoint of the titration, the concentration of the weak acid is equal to the concentration of its conjugate base. This point is also known as half-neutralization because half the acid has been neutralized by the strong base.

c. At the equivalence point the pH is greater than 7 because the acid (HA) has been converted to its conjugate base (A^-) by sodium hydroxide and equilibrium moves backward toward the acid and produces hydroxide:

$$A^- + H_2O \rightleftharpoons AH + OH^-$$

d. When the excess titrant has been added the solution becomes basic because sodium hydroxide completely neutralized the weak acid.

7.

a. The titration begins with a pH that is lower than the titration of a strong base but higher than the $pH = 7$. At the beginning of the titration, there is a sharp decrease in pH because the cation of the weak base becomes a common ion that reduces the ionization of the base.

b. The sharp decrease at the beginning of the titration changes gradually due to the solution becoming a buffer. This continues until the strong acid has overcome the buffer capacity. At the midpoint of the titration, the concentration of the weak base is equal to the concentration of its conjugate acid $pH = pK_a$. This point is also known as half-neutralization because half the base has been neutralized by the strong acid.

c. At the equivalence point the pH is less than 7 because the base NH_3 has been converted to its conjugate acid NH_4^+ by hydrochloric acid and equilibrium moves forwards toward the base and produces NH_4Cl^-:

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

d. When excess titrant has been added the solution becomes acidic because hydrochloric acid completely neutralized the weak base.

8.

$$HA \overset{K_a}{\rightleftharpoons} A^- + H^+$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$pH = pK_a + log(\frac{[A^-]}{[HA]}$$

Assume $[A^-] = [HA] = 1$

$$pH = pK_a + log(1)$$

$$pH = pK_a + 0$$

$$pH = pK_a$$

9. Electronic methods are preferred over chemical indicators because it is a more accurate method at determining the pH. Also, chemical indicators must be selected to observe a narrow pH range while electronic methods observe a wider range.

10.

Ammonia is a weak base and dissociates in water as:

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

When NH_4Cl is added, it 100% dissociates into NH_4^+ and Cl^- in water:

$$NH_4Cl\,(aq) \rightleftharpoons NH_4^+\,(aq) + Cl^-\,(aq)$$

Due to common ion, $NH_4^+\,(aq)$ the dissociation of NH_3 will decrease. Thus, the concentration of $OH^-\,(aq)$ decreases and the concentration of H_3O^+ increases.

Since $pH = -log(H_3O^+)$ the pH and H_3O^+ are inversely related, the concentration of H_3O^+ concentration increases and pH decreases.

11.

a. The position of equilibrium shift to the left and the pH decreases.

b. The position of equilibrium shifts to the right and the pH increases.

c. The position of equilibrium shifts to the left and the pH increases.

12.

a. The position of equilibrium shifts to the left and the pH decreases.

b. The position of equilibrium shifts to the left and the pH increases.

c. The position of equilibrium shifts to the left and the pH increases.

Numerical Problems

1. Calculate the pH of each solution.

a. A volume of 25.0 mL of 6.09 M HCl is added to 100.0 mL of distilled water
b. A volume of 5.0 mL of 2.55 M $NaOH$ is added to 75.0 mL of distilled water.

2. What is the pH of a solution prepared by mixing 50.0 mL of 0.225 M HCl with 100.0 mL of a 0.184 M solution of $NaOH$?

3. What volume of 0.50 M HCl is needed to completely neutralize 25.00 mL of 0.86 M $NaOH$?

4.Calculate the final pH when each pair of solutions is mixed.

a. 100 mL of 0.105 M HCl and 100 mL of 0.115 M sodium acetate
b. 50 mL of 0.10 M HCl and 100 mL of 0.15 M sodium acetate
c. 100 mL of 0.109 M acetic acid and 100 mL of 0.118 M $NaOH$
d. 100 mL of 0.998 M acetic acid and 50.0 mL of 0.110 M $NaOH$

5. Calculate the final pH when each pair of solutions is mixed.

a. 100 mL of 0.983 M HCl and 100 mL of 0.102 M sodium fluoride
b. 50.0 mL of 0.115 M HCl and 100 mL of 0.109 M sodium fluoride
c. 100 mL of 0.106 M hydrofluoric acid and 50.0 mL of 0.996 M $NaOH$
d. 100 mL of 0.107 M sodium acetate and 50.0 mL of 0.987 M acetic acid

6. Calcium carbonate is a major contributor to the "hardness" of water. The amount of CaCO3 in a water sample can be determined by titrating the sample with an acid, such as HCl, which produces water and CO2. Write a balanced chemical equation for this reaction. Generate a plot of solution pH versus volume of 0.100 M HCl added for the titration of a solution of 250 mg of CaCO3 in 200.0 mL of water with 0.100 M HCl; assume that the HCl solution is added in 5.00 mL increments. What volume of HCl corresponds to the equivalence point?

7. For a titration of 50.0 mL of 0.288 M $NaOH$, you would like to prepare a 0.200 M HCl solution. The only HCl solution available to you, however, is 12.0 M.

a. How would you prepare 500 mL of a 0.200 M HCl solution?
b. Approximately what volume of your 0.200 M HCl solution is needed to neutralize the $NaOH$ solution?
c. After completing the titration, you find that your "0.200 M" HCl solution is actually 0.187 M. What was the exact volume of titrant used in the neutralization?

8. While titrating 50.0 mL of a 0.582 M solution of HCl with a solution labeled "0.500 M KOH," you overshoot the endpoint. To correct the problem, you add 10.00 mL of the HCl solution to your flask and then carefully continue the titration. The total volume of titrant needed for neutralization is 71.9 mL.

a. What is the actual molarity of your KOH solution?
b. What volume of titrant was needed to neutralize 50.0 mL of the acid?

9. Complete the following table and generate a titration curve showing the pH versus volume of added base for the titration of 50.0 mL of 0.288 M HCl with 0.321 M $NaOH$. Clearly indicate the equivalence point.

Base Added (mL)	10.0	30.0	40.0	45.0	50.0	55.0	65.0	75.0
pH								

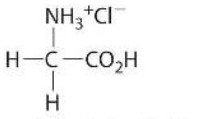
10. The following data were obtained while titrating 25.0 mL of 0.156 M $NaOH$ with a solution labeled "0.202 M HCl." Plot the pH versus volume of titrant added. Then determine the equivalence point from your graph and calculate the exact concentration of your HCl solution.

Volume of HCl (mL)	5	10	15	20	25	30	35
pH	11.46	11.29	10.98	4.40	2.99	2.70	2.52

11. Fill in the data for the titration of 50.0 mL of 0.241 M formic acid with 0.0982 M KOH. The pKa of formic acid is 3.75. What is the pH of the solution at the equivalence point?

Volume of Base Added (mL)	0	5	10	15	20	25
pH						

12. Glycine hydrochloride, which contains the fully protonated form of the amino acid glycine, has the following structure:



glycine hydrochloride

It is a strong electrolyte that completely dissociates in water. Titration with base gives two equivalence points: the first corresponds to the deprotonation of the carboxylic acid group and the second to loss of the proton from the ammonium group. The corresponding equilibrium equations are as follows:

$$^{+}NH_3 - CH_2 - CO_2H\,(aq) \rightleftharpoons \quad pK_{a1} = 2.3 \tag{4.E.2}$$

$$^{+}NH_3 - CH_2 - CO_2\,(aq) + H^{+} \tag{4.E.3}$$

$$^{+}NH_3 - CH_2 - CO_2\,(aq) \rightleftharpoons \quad pK_{a2} = 9.6 \tag{4.E.4}$$

$$NH_2 - CH_2 - COO\,(aq) + H^{+} \tag{4.E.5}$$

Given 50.0 mL of solution that is 0.430 M glycine hydrochloride, how many milliliters of 0.150 M KOH are needed to fully deprotonate the carboxylic acid group?

a. How many additional milliliters of KOH are needed to deprotonate the ammonium group?
b. What is the pH of the solution at each equivalence point?
c. How many milliliters of titrant are needed to obtain a solution in which glycine has no net electrical charge? The pH at which a molecule such as glycine has no net charge is its isoelectric point. What is the isoelectric point of glycine?

13. What is the pH of a solution prepared by adding 38.2 mL of 0.197 M HCl to 150.0 mL of 0.242 M pyridine? The pKb of pyridine is 8.77.

14. What is the pH of a solution prepared by adding 40.3 mL of 0.289 M $NaOH$ to 150.0 mL of 0.564 M succinic acid ($HO_2CCH_2CH_2CO_2H$)? (For succinic acid, pKa1 = 4.21 and pKa2 = 5.64).

14. Calculate the pH of a 0.15 M solution of malonic acid ($HO_2CCH_2CO_2H$), whose pKa values are as follows: pKa1 = 2.85 and pKa2 = 5.70.

Answers

1.

a.$pH = -log([H_3O^{+}]) = -log(1.218) = -0.086$

$[HCl] = [H^{+}]$

$M_1V_1 = M_2V_2 \rightarrow (6.09\,M)(25\,mL) = (x)(125\,mL) \rightarrow x = 1.218$

b. $pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 0.80 = 13$

$pOH = -log([OH^{-}]) = -log(0.159) = 0.80$

$[NaOH] = [OH^{-}]$

$M_1V_1 = M_2V_2 \rightarrow (2.55\,M)(5.0\,mL) = (x)(80\,mL) \rightarrow x = 0.159$

2.

$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - 1.321 = 12.7$

$HCl : 50.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.225\,mol}{1\,L} = 0.01125\,mol$

$NaOH : 100.0\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.184\,mol}{1\,L} = 0.0184\,mol$

Note the number of moles for $NaOH$ is greater than HCl, therefore we calculate pOH.

$0.0184 - 0.01125 = 0.00715\,mol$

$\frac{0.00715\,mol}{.15\,L} = 0.0477$

$pOH = -log([OH^-]) = -log(0.0477) = 1.321$

3. $M_1V_1 = M_2V_2 \rightarrow (0.50\,M)(x\,L) = (0.86\,M)(0.25\,L) \rightarrow x\,L = 4.3 \times 10^{-2}\,L$

4. Video Solution

a. $pH = pK_a + log(\frac{C_2H_3NaO_2}{C_2H_4O_2}) = 4.76 + log(\frac{0.0935}{0.0105}) = 5.71$

$HCl: 100\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.0105\,mol}{1\,L} = 0.0105\,mol$

$C_2H_3NaO_2: 100\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.115\,mol}{1\,L} = 0.0115\,mol$

$C_2H_3NaO_2\,(s) + HCl\,(aq) \rightarrow C_2H_4O_2\,(aq) + NaCl\,(s)$

	$C_2H_3NaO_2$	HCl	$C_2H_4O_2$	$NaCl$
I	0.0115	0.0105	0	-
C	-0.0105	-0.0105	+0.0105	-
E	0.0935	0	0.0105	-

b. $pH = pK_a + log(\frac{C_2H_3NaO_2}{C_2H_4O_2}) = 4.76 + log(\frac{0.01}{0.005}) = 5.05$

$HCl: 100\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.0105\,mol}{1\,L} = 0.005\,mol$

$C_2H_3NaO_2: 100\,mL \times \frac{1\,L}{1{,}000\,mL} \times \frac{0.115\,mol}{1\,L} = 0.015\,mol$

$C_2H_3NaO_2\,(s) + HCl\,(aq) \rightarrow C_2H_4O_2\,(aq) + NaCl\,(s)$

	$C_2H_3NaO_2$	HCl	$C_2H_4O_2$	$NaCl$
I	0.015	0.005	0	0
C	-0.005	-0.005	+0.005	+0.005
E	0.01	0	0.005	0.005

c. $pH = 14 - pOH = 14 - (-log(\frac{0.0118-0.0109}{0.2\,L})) = 11.7$

$CH_3COOH: 0.1\,L \times 0.109\,M = 0.0109\,mol$

$NaOH: 0.1\,L \times 0.118\,M = 0.0118\,mol$

$CH_3COOH\,(aq) + NaOH\,(aq) \rightarrow H_2O\,(l) + CH_3COO^-Na\,(aq)$

	CH_3COOH	$NaOH$	H_2O	CH_3COONa
I	0.0109	0.0118	-	0
C	-0.0109	-0.0109	-	+0.0109
E	0	9×10^{-4}	-	0.0109

d. $pH = 4.76 + log(\frac{0.0055}{0.0943}) = 3.53$

$CH_3COOH: 0.1\,L \times 0.998\,M = 0.0998\,mol$

$NaOH: 0.05\,L \times 0.110\,M = 0.0055\,mol$

$CH_3COOH\,(aq) + NaOH\,(aq) \rightarrow H_2O\,(l) + CH_3COONa\,(aq)$

	CH_3COOH	$NaOH$	H_2O	CH_3COONa
I	0.0998	0.0055	-	0
C	-0.0055	-0.0055	-	+0.0055
E	0.0943	0	-	0.0055

5. Video Solution

a. $pH = -log(\frac{0.9728}{0.2\,L}) = 4.86$

$HCl: 100\,mL \times \frac{1\,L}{1{,}000\,L} \times 0.983\,M = 0.983\,mol$

$NaF: 100\,mL \times \frac{1\,L}{1{,}000\,L} \times 0.102\,M = 0.0102\,mol$

$HCl\,(aq) + NaF\,(s) \rightarrow NaCl\,(aq) + HF\,(aq)$

	HCl	NaF	$NaCl$	HF
I	0.983	0.0102	-	0
C	-0.0102	-0.0102	-	-0.0102
E	0.9728	0	-	-0.0102

b. $pH = pK_a + log(\frac{[NaF]}{[HF]}) = 3.14 + log(\frac{0.00515}{0.00575}) = 3.09$

$HCl: 50\,mL \times \frac{1\,L}{1{,}000\,L} \times 0.115\,M = 0.00575\,mol$

$NaF: 100\,mL \times \frac{1\,L}{1{,}000\,L} \times 0.109\,M = 0.0109\,mol$

$HCl\,(aq) + NaF\,(s) \rightarrow NaCl\,(aq) + HF\,(aq)$

	HCl	NaF	$NaCl$	HF
I	0.00575	0.0109	-	0
C	-0.00575	-0.00575	-	+0.00575
E	0	0.00515	-	0.00575

c. $pH = 14 - pOH = 14 - (-log(0.0498 - 0.0106)) = 12.6$

$HF: 100\,mL \times \frac{1\,L}{1{,}000\,L} \times 0.106\,M = 0.0106\,mol$

$NaOH: 50\,mL \times \frac{1\,L}{1{,}000\,L} \times 0.996\,M = 0.0498\,mol$

$HF\,(aq) + NaOH\,(aq) \rightarrow NaF\,(aq) + H_2O\,(aq)$

$HCl(aq) + NaOH(aq) \rightarrow NaCl\,(aq) + H_2O$

d. $pH = pK_a + log(\frac{[C_2H_3NaO_2]}{[CH_3COOH]}) = 4.76 + log(\frac{0.0107}{0.04935}) = 4.10$

$C_2H_3NaO_2: 0.1\,L \times 0.107\,M = 0.0107$

$CH_3COOH: 0.05\,mL \times 0.987\,M = 0.04935$

$CH_3COOH\,(aq) + H_2O \rightarrow C_2H_3O^- + H_3O^+$

6.

$CaCO_3\,(aq) + 2\,HCl\,(aq) \rightarrow CaCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$

$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$

$HCO_3^{2-}(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$

$K_{a1} = 4.3 \times 10^{-7}$

$K_{a2} = 5.0 \times 10^{-11}$

At 0 mL addition of HCl: $pH = 14 - pOH = 14 - (-log(\sqrt{0.0125 \times \frac{10^{-14}}{5.0 \times 10^{-11}}}) = 11.20$

$CaCO_3 : 250\ mg \times \frac{1\ g}{1{,}000\ mg} \times \frac{1\ mol}{100.0869\ g} \times \frac{1}{200\ mL \times \frac{1\ L}{1{,}000\ mL}} = 0.0125\ M$

At 5 mL addition of HCl: $pH = -log(5 \times 10^{-11}) + log(\frac{0.002}{0.0005}) = 10.9$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.005\ L \times 0.1\ M = 0.0005\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.0005	0
C	-0.0005	-0.0005	0.0005
E	0.002	0	0.0005

At 10 mL addition of HCl: $pH = -log(5 \times 10^{-11}) + log(\frac{0.001}{0.0015}) = 10.5$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.01\ L \times 0.1\ M = 0.001\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.001	0
C	-0.001	-0.001	0.001
E	0.0015	0	0.001

At 15 mL addition of HCl:$pH = -log(5 \times 10^{-11}) + log(\frac{0.001}{0.0015}) = 10.1$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl : 0.015\ L \times 0.1\ M = 0.0015\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.0015	0
C	-0.0015	-0.0015	0.0015
E	0.001	0	0.0015

At 20 mL addition of HCl:$pH = -log(5 \times 10^{-11}) + log(\frac{5 \times 10^{-4}}{0.002}) = 9.7$

$CaCO_3 : 0.2\ L \times 0.0125\ M = 0.0025\ mol$

$HCl: 0.02\,L \times 0.1\,M = 0.002\,mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.002	0
C	-0.002	-0.002	0.002
E	5×10^{-4}	0	0.002

At 25 mL addition of HCl: first equivalence point: $pH = \frac{-log(K_{a1})-log(K_{a2})}{2} = \frac{-log(4.3\times10^{-7})-log(5.0\times10^{-11})}{2} = 8.33$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.025\,L \times 0.1\,M = 0.0025\,mol$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0025	0
C	-0.0025	-0.0025	0.0025
E	0	0	0.0025

At 30 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.0005}) = 7.07$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.03\,L \times 0.1\,M = 0.003$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.003	0
C	-0.0025	-0.0025	0.0025
E	0	5×10^{-4}	0.0025

At 35 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.001}) = 6.76$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.035\,L \times 0.1\,M = 0.0035$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0035	0
C	-0.0025	-0.0025	0.0025
E	0	0.001	0.0025

At 40 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.003}) = 6.59$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.040\ L \times 0.1\ M = 0.004$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.004	0
C	-0.0025	-0.0025	0.0025
E	0	0.0015	0.0025

At 45 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.002}) = 6.46$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.045\ L \times 0.1\ M = 0.0045$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0045	0
C	-0.0025	-0.0025	0.0025
E	0	0.002	0.0025

At 50 mL addition of HCl: second equivalence point: $pH = 3.86$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.05\ L \times 0.1\ M = 0.005$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.005	0
C	-0.0025	-0.0025	0.0025
E	0	0.0025	0.0025

At 55 mL addition of HCl: $pH = -log(\frac{0.003}{0.055}) = 1.26$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.055\ L \times 0.1\ M = 0.0055$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0055	0
C	-0.0025	-0.0025	0.0025
E	0	0.003	0.0025

At 60 mL addition of HCl: $pH = -log(\frac{0.0035}{0.06}) = 1.23$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.06\,L \times 0.1\,M = 0.006$

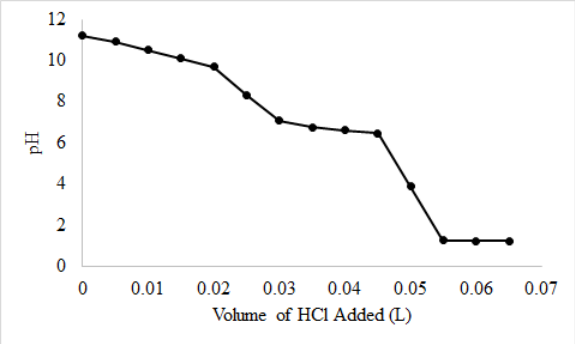
	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.006	0
C	-0.0025	-0.0025	0.0025
E	0	0.0035	0.0025

At 65 mL addition of HCl: $pH = -log(\frac{0.0040}{0.065}) = 1.21$

$HCO_3^-: 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl: 0.06\,L \times 0.1\,M = 0.006$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0065	0
C	-0.0025	-0.0025	0.0025
E	0	0.0040	0.0025



7. Video Solution

a. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{V_2} = \frac{(0.2\,M)(0.5\,L)}{12.0\,M} = 8.33 \times 10^{-3}\,L$ Therefore, dilute 8.33 mL of 12.0 M HCl to 500.0 mL.

b. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{V_2} = \frac{(0.288\,M)(0.05\,L)}{0.2\,M} = 7.20 \times 10^{-3}\,L$

c. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{V_2} = \frac{(0.288\,M)(0.05\,L)}{0.187\,M} = 7.70 \times 10^{-2}$

8.

a. $M_1V_1 = M_2V_2 \rightarrow M_2 = \frac{M_1V_1}{V_2} = \frac{(0.582\,M)(0.060\,L)}{0.0719\,L} = 0.49\,M$

b. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V_1}{M_2} = \frac{(0.582\,M)(0.050\,L)}{0.49\,M} = 59.4 \times 10^{-2}\,L$

9.

Volume of Base Added (mL)	10.0	30.0	40.0	45.0	50.0	55.0	65.0	75.0
pH	0.73	1.22	1.76	7	12.2	12.5	13.0	13.1

$NaOH\,(aq) + HCl\,(aq) \rightarrow NaCl\,(s) + H_2O\,(l)$

At 0 mL of base added: $pH = -log(0.288) = 0.54$

At 10 mL of base added: $pH = -log(\frac{0.0144 - 0.00321}{0.06}) = 0.73$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.01\ L \times 0.321\ M = 0.00321$

At 30 mL of base added: $pH = -log(\frac{0.0144-0.00963}{0.08}) = 1.22$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.03\ L \times 0.321\ M = 0.00963$

At 40.0 mL of base added: $pH = -log(\frac{0.0144-0.01284}{0.09}) = 1.76$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.04\ L \times 0.321\ M = 0.01284$

At 45.0 mL of base added: $pH = 7$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.045\ L \times 0.321\ M = 0.0144$

All HCl will neutralize at the equivalence point $[H^+] = [OH^-]$ and the pH of the solution is 7.

At 50.0 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.01605-0.0144}{0.1}) = 12.2$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.050\ L \times 0.321\ M = 0.01605$

At 55 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.01605-0.0144}{0.1}) = 12.5$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.055\ L \times 0.321\ M = 0.017655$

At 65 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.020865-0.0144}{0.07}) = 13.0$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.065\ L \times 0.321\ M = 0.020865$

At 75 mL base added: $pH = 14 - pOH = 14 - log(\frac{0.024075-0.0144}{0.08}) = 13.1$

$HCl: 0.05\ L \times 0.288\ M = 0.0144$

$NaOH: 0.075\ L \times 0.321\ M = 0.024075$

10.



The equivalence point is at pH 7 and this occurs at 0.0193 L.

$V_2 = \frac{(0.156\ M)(0.025\ L)}{0.202} = 0.0193\ L$

11.

pH at equivalence point: $14 - (-log\sqrt{(\frac{10^{-14}}{10^{-3.75}} \times \frac{0.01205}{0.05+0.1227})}) = 8.30$

$0.05\ L \times 0.241\ M = 0.01205\ mol$

$V_2 = \frac{(0.05\ L)(0.241\ M)}{0.0982} = 0.1227\ L$

Volume of Base Added (mL)	0	5	10	15	20	25
pH	2.18	2.38	2.70	2.89	3.04	3.16

At 0 mL of base added: $pH = -log([H^+]) = -log(2.52 \times 10^{-6}) = 2.18$

$[H^+] = \sqrt{10^{-3.75} \times 0.241\ M} = 2.52 \times 10^{-6}$

At 5 mL of base added: $pH = 3.75 + log(\frac{4.91 \times 10^{-4}}{0.01205 - 4.91 \times 10^{-4}}) = 2.38$

$KOH: 0.05\ L \times 0.0982\ M = 4.91 \times 10^{-4}\ mol$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205\ mol$

At 10 mL of base added: $pH = 3.75 + log(\frac{9.82 \times 10^{-4}}{0.01205 - 9.82 \times 10^{-4}}) = 2.70$

$KOH: 0.01\ L \times 0.0982\ M = 9.82 \times 10^{-4}\ mol$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205\ mol$

At 15 mL of base added:$pH = 3.75 + log(\frac{0.001473}{0.01205 - 0.001473} = 2.89$

$KOH: 0.015\ L \times 0.0982\ M = 0.001473$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205$

At 20 mL of base added: $pH = 3.75 + log(\frac{0.001964}{0.01205 - 0.001964}) = 3.04$

$KOH: 0.02\ L \times 0.0982\ M = 0.001964$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205$

At 25 mL base added: $pH = 3.75 + log(\frac{0.002455}{0.01205 - 0.002455}) = 3.16$

$KOH: 0.025\ L \times 0.0982\ M = 0.002455\ mol$

$CH_2O_2: 0.05\ L \times 0.241\ M = 0.01205$

12. $M_1V_1 = M_2V_2 \rightarrow V_2 = \frac{M_1V1}{M_2} = \frac{(0.430\ M)(0.05\ L)}{0.150\ M} = 1.42 \times 10^{-1}\ L$

143 mL are needed to fully deprotonate the carboxylic acid group.

a. 143 additional milliliters of KOH are needed to deprotonate the ammonium group.

b. At the first equivalence point: $pH = \frac{(pKa_1 + pKa_2)}{2} = 5.95$

c. 143 mL of titrant are needed to obtain a solution in which glycine has no electrical charge. The isoelectric point of glycine 5.95.

13.

$pH = pK_a + log(\frac{[C_5H_5N]}{[C_5H_5NH^+]}) = (14 - 8.77) + log(\frac{0.02996}{0.0063434}) = 5.90$

$C_5H_5N\ (aq) + HCl\ (aq) \rightarrow C_5H_5NH^+\ (aq) + Cl^-\ (aq)$

$HCl: 32.2\ mL \times \frac{1\ L}{1{,}000\ mL} \times 0.197\ M = 0.0063434\ mol$

$C_5H_5N : 150\,mL \times \frac{1\,L}{1{,}000\,mL} \times 0.242\,M = 0.0363\,mol$

	C_5H_5N	HCl	$C_5H_5NH^+$	Cl^-
I	0.0363	0.0063434	0	-
C	-0.0063434	-0.0063434	+0.0063434	-
E	0.02996	0	0.0063434	-

14. $pH = \frac{(4.21+5.64)}{2} = 4.93$

15. $pH = \frac{(2.85+5.70)}{2} = 4.25$

17.4: Solubility Equilibria

Conceptual Problems

1. Write an expression for K_{sp} for each salt.

a. AgI
b. CaF_2
c. $PbCl_2$
d. Ag_2CrO_4

2. Some species are not represented in a solubility product expression. Why?

3. Describe the differences between Q and K_{sp}.

4. How can an ion product be used to determine whether a solution is saturated?

5. When using K_{sp} to directly compare the solubilities of compounds, why is it important to compare only the K_{sp} values of salts that have the same stoichiometry?

6. Describe the effect of a common ion on the solubility of a salt. Is this effect similar to the common ion effect found in buffers? Explain your answer.

7. Explain why the presence of $MgCl_2$ decreases the molar solubility of the sparingly soluble salt $MgCO_3$.

Conceptual Answers

1.

a. $K_{sp} = [Ag^+][I^-]$

b. $K_{sp} = [Ca^{2+}][F^-]^2$

c. $K_{sp} = [Pb^{2+}][Cl^-]^2$

d. $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

2. The solubility constant expression, K_{sp} is an equilibrium constant for a solid substance dissolving in a an aqueous solution. Thus, it is a measure of solubility and species that do not dissolve are not represented in the solubility product expression.

3. The main difference between Q and K_sp is that Q describes a reaction that is not at equilibrium unlike K_{sp}.

4. An ion product can be used to determine whether a solution is saturated as it is compared to K_{sp} where there are three possible conditions for an aqueous solution of an ionic solid:

    1. $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
    2. $Q = K_{sp}$. The solution is saturated and at equilibrium.
    3. $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

5. For a 1:1 salt, the molar solubility is simply $\sqrt{K_{sp}}$; for a 2:1 salt, the molar solubility is $\sqrt[3]{K_{sp}/4}$. Consequently, the magnitudes of K_{sp} can be correlated with molar solubility only if the salts have the same stoichiometry.

6. By the presence of a common ion, the solubility of any sparingly soluble salt is always decreased. This is similar to the common ion effect found in buffers as adding a common cation or anion shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle.
7. Because of the common ion effect. Adding a soluble Mg^{2+} salt increases [Mg2+] in solution, and Le Chatelier's principle predicts that this will shift the solubility equilibrium of $MgCO_3$ to the left, decreasing its solubility.

Numerical Problems

1. Predict the molar solubility of each compound using the K_{sp} values given in Chapter 26.
    a. $Cd(IO_3)_2$
    b. $AgCN$
    c. HgI_2
2. Predict the molar solubility of each compound using the K_{sp} values given.
    a. Li_3PO_4: 2.37×10^{-11}
    b. $Ca(IO_3)_2$: 6.47×10^{-6}
    c. $Y(IO_3)_3$: 1.12×10^{-10}
3. A student prepared 750 mL of a saturated solution of silver sulfate (Ag_2SO_4). How many grams of Ag_2SO_4 does the solution contain? $K_{sp} = 1.20 \times 10^{-5}$.
4. Given the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C" and Appendix B, predict the molar concentration of each species in a saturated aqueous solution.
    a. silver bromide
    b. lead oxalate
    c. iron(II) carbonate
    d. silver phosphate
    e. copper(I) cyanide
5. Given the K_{sp} values in Table 17.1 "Solubility Products for Selected Ionic Substances at 25°C" and Appendix B predict the molar concentration of each species in a saturated aqueous solution.
    a. copper(I) chloride
    b. lanthanum(III) iodate
    c. magnesium phosphate
    d. silver chromate
    e. strontium sulfate
6. Silicon dioxide, the most common binary compound of silicon and oxygen, constitutes approximately 60% of Earth's crust. Under certain conditions, this compound can react with water to form silicic acid, which can be written as either H_4SiO_4 or $Si(OH)_4$. Write a balanced chemical equation for the dissolution of SiO_2 in basic solution. Write an equilibrium constant expression for the reaction.
7. The $K_{sp}$of $Mg(OH)_2$ is 5.61×10^{-12}. If you tried to dissolve 24.0 mg of $Mg(OH)_2$ in 250 mL of water and then filtered the solution and dried the remaining solid, what would you predict to be the mass of the undissolved solid? You discover that only 1.0 mg remains undissolved. Explain the difference between your expected value and the actual value.
8. The Ksp of lithium carbonate is 8.15×10^{-4}. If 2.34 g of the salt is stirred with 500 mL of water and any undissolved solid is filtered from the solution and dried, what do you predict to be the mass of the solid? You discover that all of your sample dissolves. Explain the difference between your predicted value and the actual value.
9. You have calculated that 24.6 mg of $BaSO_4$ will dissolve in 1.0 L of water at 25°C. After adding your calculated amount to 1.0 L of water and stirring for several hours, you notice that the solution contains undissolved solid. After carefully filtering the solution and drying the solid, you find that 22.1 mg did not dissolve. According to your measurements, what is the K_{sp} of barium sulfate?

10. In a saturated silver chromate solution, the molar solubility of chromate is 6.54×10^{-5}. What is the K_{sp}?

11. A saturated lead(II) chloride solution has a chloride concentration of 1.62×10^{-2} mol/L. What is the K_{sp}?

12. From the solubility data given, calculate K_{sp} for each compound.

    a. AgI: 2.89×10^{-7} g/100 mL
    b. SrF_2: 1.22×10^{-2} g/100 mL
    c. $Pb(OH)_2$: 78 mg/500 mL
    d. $BiAsO_4$: 14.4 mg/2.0 L

13. From the solubility data given, calculate K_{sp} for each compound.

    a. $BaCO_3$: 10.0 mg/500 mL
    b. CaF_2: 3.50 mg/200 mL
    c. $Mn(OH)_2$: 6.30×10^{-4} g/300 mL
    d. Ag_2S: 1.60×10^{-13} mg/100 mL

14. Given the following solubilities, calculate Ksp for each compound.

    a. $BaCO_3$: 7.00×10^{-5} mol/L
    b. CaF_2: 1.70 mg/100 mL
    c. $Pb(IO_3)_2$: 2.30 mg/100 mL
    d. SrC_2O_4: 1.58×10^{-7}mol/L

15. Given the following solubilities, calculate K_{sp} for each compound.

    a. Ag_2SO_4: 4.2×10^{-1} g/100 mL
    b. $SrSO_4$: 1.5×10^{-3} g/100 mL
    c. CdC_2O_4: 6.0×10^{-3} g/100 mL
    d. $Ba(IO_3)_2$: 3.96×10^{-2} g/100 mL

16. The K_{sp} of the phosphate fertilizer $CaHPO_4 \cdot 2H_2O$ is 2.7×10^{-7} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 3.0 L of water at this temperature?

17. The K_{sp} of zinc carbonate monohydrate is 5.5×10^{-11} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 2.0 L of water at this temperature?

18. Silver nitrate eye drops were formerly administered to newborn infants to guard against eye infections contracted during birth. Although silver nitrate is highly water soluble, silver sulfate has a K_{sp} of 1.20×10^{-5} at 25°C. If you add 25.0 mL of 0.015 M $AgNO_3$to 150 mL of 2.8×10^{-3} M Na_2SO_4, will you get a precipitate? If so, what will its mass be?

19. Use the data in Appendix B to predict whether precipitation will occur when each pair of solutions is mixed.

    a. 150 mL of 0.142 M $Ba(NO_3)_2$ with 200 mL of 0.089 M NaF
    b. 250 mL of 0.079 M K_2CrO_4 with 175 mL of 0.087 M $CaCl_2$
    c. 300 mL of 0.109 M $MgCl_2$ with 230 mL of 0.073 M $Na_2(C_2O_4)$

20. What is the maximum volume of 0.048 M $Pb(NO_3)_2$ that can be added to 250 mL of 0.10 M NaSCN before precipitation occurs?$K_{sp} = 2.0 \times 10^{-5}$ for $Pb(SCN)_2$.

21. Given 300 mL of a solution that is 0.056 M in lithium nitrate, what mass of solid sodium carbonate can be added before precipitation occurs (assuming that the volume of solution does not change after adding the solid)? $K_{sp} = 8.15 \times 10^{-4}$ for Li_2CO_3.

22. Given the information in the following table, calculate the molar solubility of each sparingly soluble salt in 0.95 M $MgCl_2$.

Saturated Solution	K_{sp}
$MgCO_3 \cdot 3H_2O$	2.4×10^{-6}
$Mg(OH)_2$	5.6×10^{-12}
$Mg_3(PO_4)_2$	1.04×10^{-24}

Numerical Answers

1.

a. $K_{sp} = [Cd^{2+}][IO_3]^2 \rightarrow 2.5 \times 10^{-8} = x(2x)^2 \rightarrow 2.5 \times 10^{-8} = 4x^3 \rightarrow x = 1.84 \times 10^{-3}$

b. $K_{sp} = [Ag^{+}][CN^{-}] \rightarrow 1.6 \times 10^{-14} = (x)(x) \rightarrow x = 7.73 \times 10^{-9}$

c. $K_{sp} = [Hg^{2+}][I^{-}]^2 \rightarrow 2.9 \times 10^{-29} = (x)(2x)^2 \rightarrow 1.94 \times 10^{-10}$

2.

a. $K_{sp} = [Li^{+}]^3[PO_4^{3-}] \rightarrow 2.37 \times 10^{-11} = (3x)^3(x) \rightarrow x = 9.68 \times 10^{-4}$

b. $K_{sp} = [Ca^{2+}][IO_3^{-}]^2 \rightarrow 6.47 \times 10^{-6} = (x)(2x)^2 \rightarrow 1.17 \times 10^{-2}$

c. $K_{sp} = [Y^{3+}][IO_3]^{-}]^3 \rightarrow 1.12 \times 10^{-10} = (x)(3x)^3 \rightarrow x = 1.42 \times 10^{-3}$

3. $0.750\,L \times \frac{0.0144\,mol}{1\,L} \times \frac{311.199\,g}{1\,mol} = 3.37\,g$

$K_{sp} = [Ag^{+}]^2[SO_4^{2-}] \rightarrow 1.20 \times 10^{-5} = (2x)^2(x) \rightarrow x = 0.0144$

4.

a. $K_{sp} = [Ag^{+}][Br^{-}] \rightarrow 5.35 \times 10^{-13} = (x)(x) \rightarrow x = 7.31 \times 10^{-7}$

b. $K_{sp} = [PB^{2+}][C_2O_4] \rightarrow 8.5 \times 10^{-9} = (x)(x) \rightarrow x = 9.2 \times 10^{-5}$

c. $K_{sp} = [Fe^{2+}][CO_3^{2-}] \rightarrow 3.13 \times 10^{-11} = (x)(x) \rightarrow x = 5.60 \times 10^{-6}$

d. $K_{sp} = [Ag^{+}]^3[PO_4^{3-}] \rightarrow 8.89 \times 10^{-17} = (3x)^3(x) \rightarrow x = 4.26 \times 10^{-5}$

e. $K_{sp} = [Cu][CN] \rightarrow 3.47 \times 10^{-20} = (x)(x) \rightarrow x = 1.86 \times 10^{-10}$

5.

a. $K_{sp} = [Cu][CN] \rightarrow 1.72 \times 10^{-20} = (x)(x) \rightarrow x = 4.15 \times 10^{-4}$

b. $K_{sp} = [La^{3+}][IO_3^{-}]^3] \rightarrow 7.50 \times 10^{-12} = (x)(3x)^3 \rightarrow x = 7.26 \times 10^{-4}$

c. $K_{sp} = [Mg^{2+}]^3[PO_4^{3-}]^2 \rightarrow 1.04 \times 10^{-24} = (3x)^3(2x)^2 \rightarrow x = 6.26 \times 10^{-6}$

d. $K_{sp} = [Ag^{+}]^2[CrO_4^{2-}] \rightarrow 1.12 \times 10^{-12} = (2x)^2(x) \rightarrow 6.54 \times 10^{-5}$

e. $K_{sp} = [Sr^{2+}][SO_4^{2-}] \rightarrow 3.44 \times 10^{-7} = (x)(x) \rightarrow x = 5.87 \times 10^{-4}$

6.

$SiO_2\,(g) + H_2O\,(l) \rightarrow Si(OH)_4\,(aq)$

$K_{sp} = [Si^{4+}][OH^{-}]^4$

7. 22.4 mg; a secondary reaction occurs, where OH^- from the dissociation of the salt reacts with H^+ from the dissociation of water. This reaction causes further dissociation of the salt (Le Chatelier's principle).

$K_{sp} = [Mg^{2+}][OH^{-}]^2 \rightarrow 5.61 \times 10^{-12} = (x)(2x)^2 \rightarrow x = 1.12 \times 10^{-4}$

8.

$Predicted\,mass: \frac{5.88 \times 10^{-2}\,mol}{1\,L} \times \frac{73.891\,g}{1\,mol} \times 0.5\,L = 2.17\,g$

$K_{sp} = [Li^{+}]^2[CO_3^{2-}] \rightarrow 8.15 \times 10^{-4} = (2x)^2(x) \rightarrow x = 5.88 \times 10^{-2}$

The difference between the predicted value and the actual value occurs because the carbonate from the dissociation of the salt reacts with the H^+ from the dissociation of water. This reaction causes further dissociation of the salt (Le Chatelier's principle).

9.

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (x)(x) = x^2 = (1.07 \times 10^{-5}\,M)^2 = 1.15 \times 10^{-10}$

$BaSO_4 : (24.6 - 22.1\,mg) \times \frac{1\,g}{1{,}000\,mg} \times \frac{1\,mol}{233.38\,g} \times \frac{1}{1.0\,L} = 1.07 \times 10^{-5}\,M$

10. $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2x)^2(x) = 4x^3 = 4(6.54 \times 10^{-5}) = 1.12 \times 106{-}12$

11. $K_{sp} = [Pb^{2+}][Cl^-]^2 = (x)(2x)^2 = 4x^3 = 4(3.24 \times 10^{-2})^3 = 1.70 \times 10^{-5}$

12.

a. $K_{sp} = [Ag^+][I^-] = x^2 = (1.23 \times 10^{-8})^2) = 1.52 \times 10^{-16}$

$AgI : (2.89 \times 10^{-7}\,g \times \frac{1\,mol}{234.77\,g} \times \frac{1}{0.1\,L} = 1.23 \times 10^{-8}$

b. $K_{sp} = [Sr^{2+}][F^-]^2] = (x)(2x)^2 = 4x^3 = 4(9.72 \times 10^{-4})^3 = 3.66 \times 10^{-9}$

$SrF_2 = 1.22 \times 10^{-2}\,g \times \frac{1\,mol}{125.62\,g} \times \frac{1}{0.1\,L} = 9.72 \times 10^{-4}$

c. $K_{sp} = [Pb^{2+}][OH^-]^2 = 4x^3 = 4(6.47 \times 10^{-4})^3 = 1.08 \times 10^{-9}$

$Pb(OH)_2 = 0.078\,g \times \frac{1\,mol}{241.21\,g} \times \frac{1}{0.1\,L} = 6.47 \times 10^{-4}$

d. $K_{sp} = [Bi^{3+}][AsO_4^{3-}] = x^2 = (2.05 \times 10^{-5})^2 = 4.21 \times 10^{-10}$

$BiAsO_4 = 0.0144\,g \times \frac{1\,mol}{350.924\,g} \times \frac{1}{2\,L} = 2.05 \times 10^{-5}$

13.

a. $K_{sp} = [Ba^{2+}][CO_3^{2-}] = x^2 = (1.01 \times 10^{-4})^2 = 1.03 \times 10^{-8}$

$BaCO_3 : 0.01\,g \times \frac{1\,mol}{197.34\,g} \times \frac{1}{0.5\,L} = 1.01 \times 10^{-4}$

b. $K_{sp} = [Ca^{2+}][F^-]^2 = 4x^3 = 4(2.24 \times 10^{-4})^3 = 4.51 \times 10^{-11}$

$CaF_2 : 0.0035\,g \times \frac{1\,mol}{78.07\,g} \times \frac{1}{0.2\,L} = 2.24 \times 10^{-4}$

c. $K_{sp} = [Mn^{2+}][OH^-]^2 = 4x^3 = 4(2.36 \times 10^{-5})^3 = 5.26 \times 10^{-14}$

$Mn(OH)_2 : 6.30 \times 10^{-4}\,g \times \frac{1\,mol}{88.95\,g} \times \frac{1}{0.3\,L} = 2.36 \times 10^{-5}$

d. $K_{sp} = [Ag^+]^2[S^{2-}] = 4x^3 = 4(6.46 \times 10^{-18})^3 = 1.08 \times 10^{-51}$

$Ag_2S : 1.60 \times 10^{-16}\,g \times \frac{1\,mol}{247.8\,g} \times \frac{1}{0.1\,L} = 6.46 \times 10^{-18}$

14.

a. $K_{sp} = [Ba^{2+}][CO_3^{2-}] = x^2 = (7.0 \times 10^{-5})^2 = 4.90 \times 10^{-9}$

b. $K_{sp} = [Ca^{2+}][F^-]^2 = 4x^3 = 4(2.18 \times 10^{-4})^3 = 4.13 \times 10^{-11}$

$CaF_2 : 0.0017\,g \times \frac{1\,mol}{78.07\,g} \times \frac{1}{0.1\,L} = 2.18 \times 10^{-4}$

c. $K_{sp} = [Pb^{2+}][IO_3^-]^2 = 4x^3 = 4(4.13 \times 10^{-5})^3 = 2.82 \times 10^{-13}$

$Pb(IO_3)_2 : 0.0023\,g \times \frac{1\,mol}{557.0053\,g} \times \frac{1}{0.1\,L} = 4.13 \times 10^{-5}$

d. $K_{sp} = [Sr^{2+}][C_2O_4^{2-}] = x^2 = (1.58 \times 10^{-7})^2 = 2.50 \times 10^{-14}$

15.

a. $K_{sp} = [Ag^+]^2[SO_4]^{2-} = 4x^3 = 4(1.35 \times 10^{-2})^3 = 9.8 \times 10^{-6}$

$Ag_2SO_4 : 4.2 \times 10^{-1}\,g \times \frac{1\,mol}{311.799\,g} \times \frac{1}{0.1\,L} = 1.35 \times 10^{-2}$

b. $K_{sp} = [Sr^{2+}][SO_4^{2-}] = x^2 = (8.17 \times 10^{-5})^2 = 6.7 \times 10^{-9}$

$SrSO_4 : 1.5 \times 10^{-3}\,g \times \frac{1\,mol}{183.68\,g} \times \frac{1}{0.1\,L} = 8.17 \times 10^{-5}$

c. $K_{sp} = [Cd^{2+}][C_2O_4^{2-}] = x^2 = (2.99 \times 10^{-4})^2 = 8.9 \times 10^{-8}$

$CdC_2O_4 : 6.0 \times 10^{-3}\, g \times \frac{1\, mol}{200.43\, g} \times \frac{1}{0.1\, L} = 2.99 \times 10^{-4}$

d. $K_{sp} = [Ba^{2+}][IO_3^-]^2 = 4x^3 = 4(8.13 \times 10^{-4})^3 = 2.15 \times 10^{-9}$

$Ba(IO_3)_2 : 3.96 \times 10^{-2}\, g \times \frac{1\, mol}{487.15\, g} \times \frac{1}{0.1\, L} = 8.13 \times 10^{-4}$

16.

$K_{sp} = [Ca^{2+}][HPO_4^{2-}] \rightarrow 2.7 \times 10^{-7} = x^2 \rightarrow x = 5.2 \times 10^{-4}$

$CaHPO4 \cdot 2H2O : 3.0\, L \times \frac{2.7 \times 10^{-7}\, mol}{1\, L} \times \frac{290.1299\, g}{1\, mol} = 2.35 \times 10^{-4}\, g$

17.

$K_{sp} = [Zn^{2+}][CO_3^{2+}] \rightarrow 5.5 \times 10^{-11} = x^2 \rightarrow x = 7.4 \times 10^{-6}$

2.1 mg

18. $Q = [Ag^+]^2[SO_4^{2-}] = (2.14 \times 10^{-3})^2 \times 2.4 \times 10^{-3} = 1.1 \times 10^{-8} < 1.20 \times 10^{-5}$ Therefore, no precipitate will form.

$Ag^+ : \frac{(0.025\, L)(0.015\, M)}{0.175\, L} = 2.14 \times 10^{-3}$

$SO_4^{2-} : \frac{(0.15\, L)(2.8 \times 10^{-3}}{0.175\, L} = 2.4 \times 10^{-3}$

19.

a. $Q = [Ba^{2+}][F^-]^2 = (0.060857)(0.05643)^2 = 1.94 \times 10^{-4} > 1.84 \times 10^{-7}$ Therefore, precipitate will form.

$Ba^{2+} : \frac{(0.150)(0.142)}{0.35} = 0.060857$

$F^- : \frac{(0.25)(0.079)}{0.35} = 0.05643$

b. \(Q=[K^{+}][Cl^{-}]=(0.0465)(0.0358)=1.66 \times 10^{-3}<21.7. Therefore, precipitate will not form.

$K^+ : \frac{(0.25)(0.079)}{0.425} = 0.0465$

$Cl^- : \frac{(0.175)(0.087)}{0.425} = 0.0358$

c. $Q = [Mg^{2+}][C_2O_4^{2-}] = (0.0617)(0.0317) = 1.95 \times 10^{-3} > 8.5 \times 10^{-5}$ Therefore, precipitate will form.

$Mg^{2+} : \frac{(0.3)(0.109)}{0.53} = 0.0617$

$C_2O_4 : \frac{(0.23)(0.073)}{0.53} = 0.0317$

20. 520 mL

21. 8.27 g

22.

a. $K_{sp} = \sqrt{2.4 \times 10^{-6}} = 1.55 \times 10^{-3}$

b. $K_{sp} = (\frac{5.6 \times 10^{-12}}{4})^{\frac{1}{3}} = 1.12 \times 10^{-4}$

c. $K_{sp} = (\frac{1.04 \times 10^{-24}}{108})^{\frac{1}{5}} = 6.26 \times 10^{-6}$

17.5: Factors that Affect Solubility

Conceptual Problems

1. Do you expect the actual molar solubility of $LaPO_4$ to be greater than, the same as, or less than the value calculated from its K_{sp}? Explain your reasoning.
2. Do you expect the difference between the calculated molar solubility and the actual molar solubility of $Ca_3(PO_4)_2$ to be greater than or less than the difference in the solubilities of $Mg_3(PO_4)_2$? Why?
3. Write chemical equations to describe the interactions in a solution that contains $Mg(OH)_2$, which forms ion pairs, and in one that contains propanoic acid ($CH_3CH_2CO_2H$), which forms a hydrated neutral molecule.
4. Draw representations of $Ca(IO_3)_2$ in solution

a. as an ionic solid.
b. in the form of ion pairs.
c. as discrete ions.

Conceptual Answers

1. It is expected that the molar solubility of \LaPO_{4}\) be less than the value from its K_{sp} because the $K_{sp} = [La^{3+}][PO_4^{3-}] = x^2$ in which the molar solubility would be the square root of of K_{sp}.

2. It would be expected that there would be no difference in the calculated molar solubility and actual molar solubility of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ follow the similar equation: $K_{sp} = 108x^5$. It would ultimately depend on the K_{sp} values as \(x= (\frac{K_{sp}}{108})^{\frac{1}{5}} in which the larger \(K_{sp} gives the larger molar solubility.

3.

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,OH^-\,(aq)$$

$$CH_3CH_2CO_2H\,(aq) \rightleftharpoons CH_3CH_2CO_2^-\,(aq) + H^+\,(aq)$$

Numerical Problem

1. Ferric phosphate has a molar solubility of 5.44 × 10^{-16} in 1.82 M Na_3PO_4. Predict its K_{sp}. The actual K_{sp} is 1.3 × 10^{-22}. Explain this discrepancy.

Numerical Answer

1. 9.90 × 10^{-16}; the solubility is much higher than predicted by K_{sp} due to the formation of ion pairs (and/or phosphate complexes) in the sodium phosphate solution.

17.6: Precipitation and Separation of Ions

Questions

1. Iron(II) hydroxide is only sparingly soluble in water at 25°C; its K_{sp} is 7.9×10^{-16}. Calculate the solubility of iron(II) hydroxide in a buffer solution with pH = 7.00.
2. A solution contains 0.60 M Ba^{2+} and 0.30 M Ca^{2+}; K_{sp} values for $BaCrO_4$ and $CaCrO_4$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. What value of $[CrO_4^{2-}]$ will result in a maximum separation of these two ions?
3. A solution contains 0.60 M Ba^{2+} and 0.30 M Ca^{2+}; K_{sp} values for $BaCrO_4$ and $CaCrO_4$ are 1.2×10^{-10} and 7.1×10^{-4} respectively. Calculate the $[Ca^{2+}]/[Ba^{2+}]$ ratio in the solution when $[CrO_4^{2-}]$ is maintained at $1.2 \times 10^{-3}\ M$.

Solutions

1. ***Answer*** $[Fe^{2+}] = 0.079$ M
   Consider...
   $[OH^-] = 10^{(-14+7)} = 1.00\text{e-}7$ (buffer).
   $[Fe^{2+}](1.00\text{e-}7)^2 = K_{sp}$; $[Fe^{2+}] = ?$
   This Fe^{2+} concentration is low; it is not very soluble in a neutral solution (pH = 7).
   What is $[Fe^{2+}]$ in a solution whose pH = 6.00?
2. ***Answer*** $[CrO_4^{2-}] = 2.37\text{e-}3$ M
   Consider...
   Solid $BaCrO_4$ will form first as $[CrO_4^{2-}]$ increases. The maximum $[CrO_4^{2-}]$ to precipitate $CaCrO_4$ is estimated as follows.
   $[CrO_4^{2-}] = \dfrac{7.1\text{e-}4}{0.30} = 2.37\text{e-}3$ M
   Estimate $[Ba^{2+}]$ when $[CrO_4^{2-}] = 2.3\text{e-}3$ M, slightly below the maximum concentration.
3. ***Answer*** $\dfrac{[Ca^2+]}{[Ba^2+]} = 3\text{e}6$
   Consider...
   $[Ba^{2+}] = \dfrac{1.2\text{e-}10}{1.2\text{e-}3} = 1\text{e-}7$;
   $\dfrac{[Ca^2+]}{[Ba^2+]} = \dfrac{0.3}{1\text{e-}7} = ?$ The ratio of three million is large!

17.7: Qualitative Analysis for Metallic Elements

Conceptual Problem

1. Given a solution that contains a mixture of $NaCl$, $CuCl_2$, and $ZnCl_2$, propose a method for separating the metal ions.

Conceptual Solution

1. Given a solution that contains a mixture of $NaCl$, $CuCl_2$, and $ZnCl_2$, we can first use H_2S to separate the Zn^{2+} through filtration, then use ZnS to separate the Cu^{2+} through filtration, and be left with Na^{+}.

4.E: Buffer, Solubility, Common Ion Effects, and Acid-Base Titration (Practice Problems with Answers) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

CHAPTER OVERVIEW

5: Thermochemistry

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All chemical changes are accompanied by the absorption or release of heat. The intimate connection between matter and energy has been a source of wonder and speculation from the most primitive times; it is no accident that fire was considered one of the four basic elements (along with earth, air, and water) as early as the fifth century BCE. In this unit we will review some of the fundamental concepts of energy and heat and the relation between them. We will begin the study of *thermodynamics*, which treats the energetic aspects of change in general, and we will finally apply this specifically to chemical change. Our purpose will be to provide you with the tools to predict the energy changes associated with chemical processes. This will build the groundwork for a more ambitious goal: to predict the direction and extent of change itself.

5.1: Spontaneous Processes

5.2: Entropy and the Second Law of Thermodynamics

5.3: The Molecular Interpretation of Entropy (3rd Law of Thermodynamics)

5.4: Gibbs Free Energy

5.4.1: Gibbs Energy practice problems

5.4.2: Free Energy and the Equilibrium Constant

5.5: Photosynthesis

5.E: Chemical Thermodynamics (Practice Problems with Answers)

Thumbnail: Dancing Flames of burning charcoal in the dark (CC BY-SA 3.0; Oscar via Wikipedia).

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5.1: Spontaneous Processes

Learning Objectives

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

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

Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure **5.1.1**).

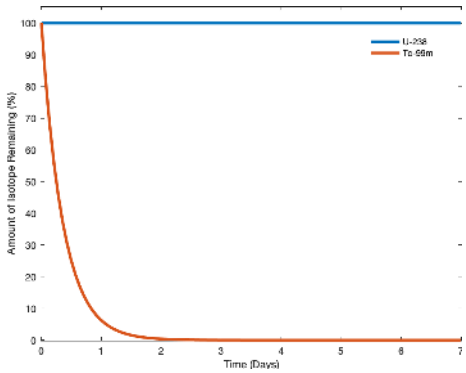


Figure **5.1.1**: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

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 **5.1.2**).

$$\mathrm{C(s,\,diamond)} \longrightarrow \mathrm{C(s,\,graphite)} \tag{5.1.1}$$

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.

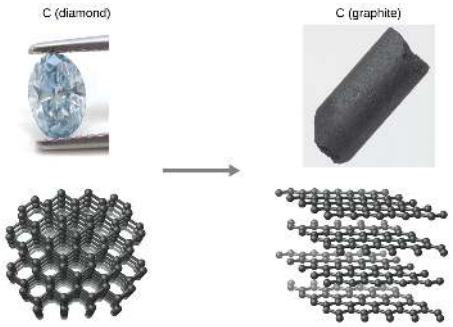


Figure **5.1.2**: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at 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 **5.1.3**). 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.

$$w = -P\Delta V \tag{5.1.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \,\mathrm{in\ a\ vaccum}) \tag{5.1.3}$$

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.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (5.1.4)$$

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).

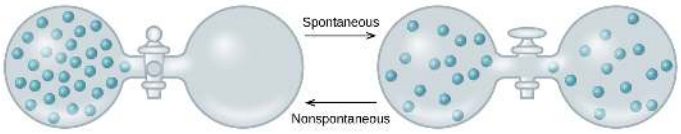


Figure **5.1.3**: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

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 **5.1.4**). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (5.1.5)$$

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 **5.1.4**: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 **5.1.1**: 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 **5.1.5**:(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 **5.1.1**

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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5.2: Entropy and the Second Law of Thermodynamics

Learning Objectives

- To understand the relationship between internal energy and entropy.

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

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

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

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are not exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure **5.2.1**.

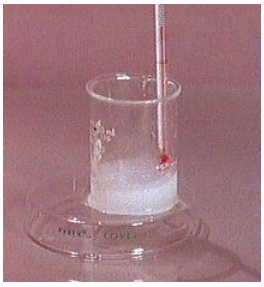


Figure **5.2.1**: An Endothermic Reaction. The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic, so water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood. For a full video: see www.youtube.com/watch?v=GQkJI-Nq3Os.

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

Entropy

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

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

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure **5.2.2**. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy.

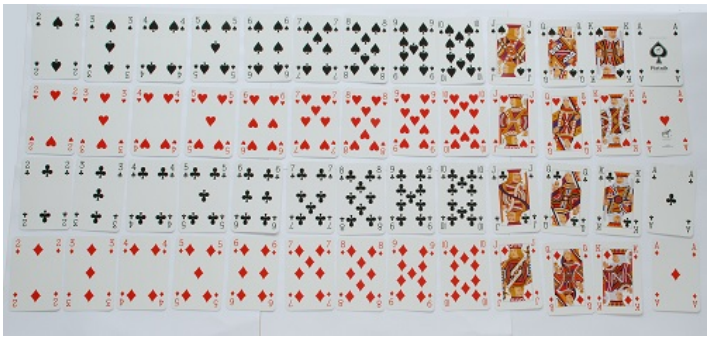


Figure **5.2.2**: Illustrating Low- and High-Entropy States with a Deck of Playing Cards. An new, unshuffled deck has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates. (CC BY-3.0 ; Trainler).

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure **5.2.3**). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure **5.2.3**, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the most probable arrangement. The others are not impossible but simply less likely.

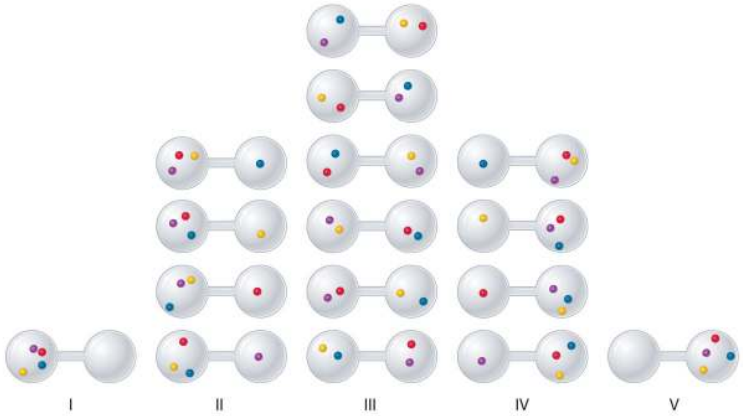


Figure **5.2.3**: The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume

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

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

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

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

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol•K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol•K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure **5.2.4**, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects increase the order of the system, leading to a decrease in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors.

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

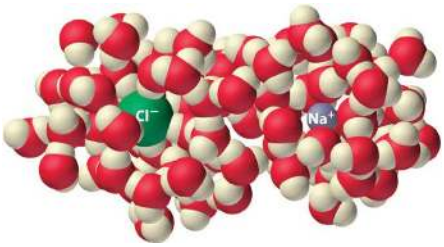


Figure 5.2.4: The Effect of Solution Formation on Entropy

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

✔ Example 5.2.1

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

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

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

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

Solution:

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

? Exercise 5.2.1

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

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

Answer a

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

Answer a

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

Video Solution

Reversible and Irreversible Changes

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

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

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{5.2.1}$$

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

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

The Relationship between Internal Energy and Entropy

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

$$q_{rev} = T\Delta S \text{ and } \Delta S = \frac{q_{rev}}{T} \tag{5.2.2}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 5.2.1 as follows:

$$\Delta U = q_{rev} + w_{rev} \tag{5.2.3}$$

$$= T\Delta S - P\Delta V \tag{5.2.4}$$

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

To illustrate the use of Equation 5.2.2 and Equation 5.2.4, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 5.2.5). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta U = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings:

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

According to Equation 5.2.4, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is

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

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

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

Thus no change in ΔS_{univ} has occurred.

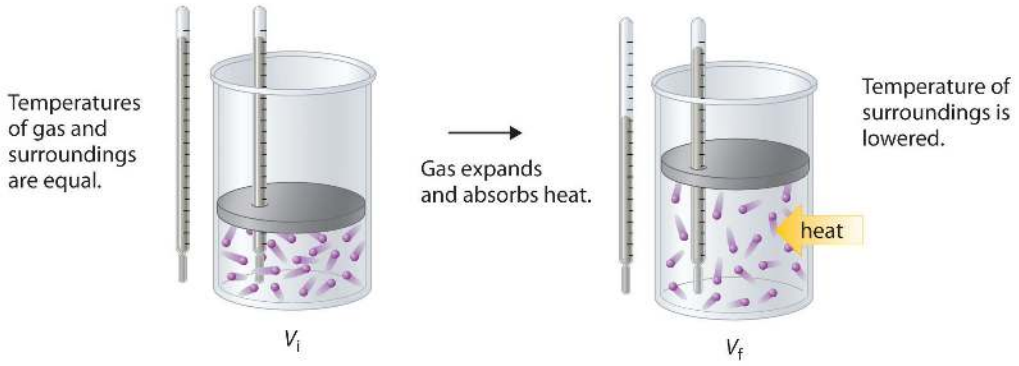


Figure **5.2.5**: Expansion of Gas at Constant Temperature

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

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

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure **5.2.6**. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 5.2.2, we see that the entropy of fusion of ice can be written as follows:

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

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

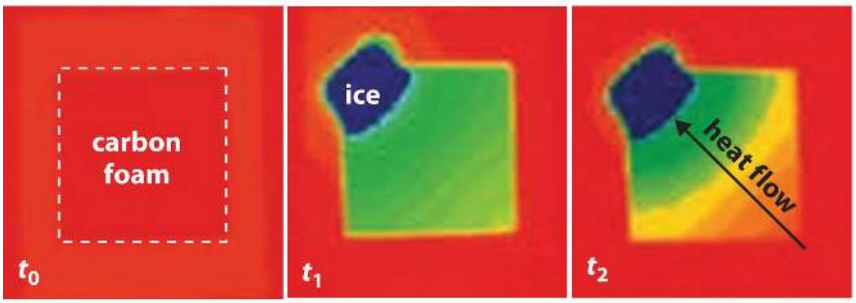


Figure **5.2.6**: Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C

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

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

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

The Second Law of Thermodynamics

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

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

$$\Delta S_{univ} = \Delta S_{cold} + \Delta S_{hot} = \frac{q}{T_{cold}} + \left(-\frac{q}{T_{hot}}\right) \tag{5.2.5}$$

The numerators on the right side of Equation 5.2.5 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} is negative will not occur as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 5.2.7).



Figure 5.2.7: Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance

Example 5.2.2: Tin Pest

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

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

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 5.2.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution

a. We know from Equation 5.2.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔU are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where q_{rev} = ΔH. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

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

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



Video 5.2.1: *Time lapse tin pest reaction.*

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

? Exercise 5.2.2

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

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

Answer a

1.09 J/(mol•K)

Answer b

S_α



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

Summary

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

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

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

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5.3: The Molecular Interpretation of Entropy (3rd Law of Thermodynamics)

Learning Objectives

- To understand entropy from a molecular interpretation

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

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

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

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

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)} \quad \Delta S < 0 \tag{5.3.1}$$

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

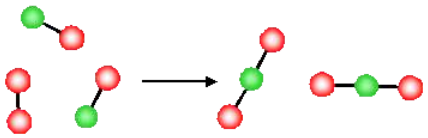


Figure 5.3.1: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

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

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

Molecular Degrees of Freedom

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 5.3.2).

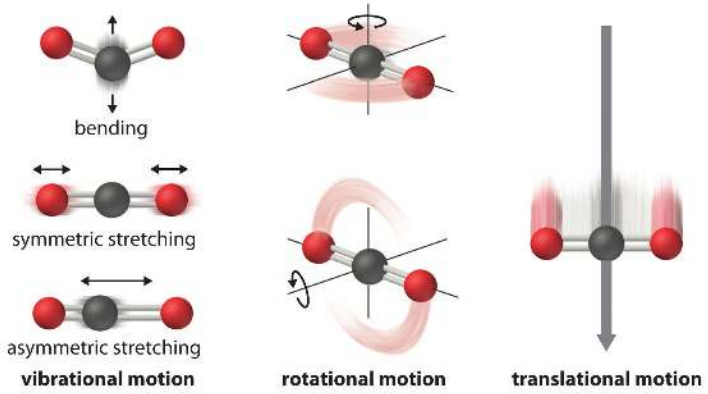


Figure **5.3.2**: Molecular Motions. Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.

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

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

The Third Law of Thermodynamics

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

The Third Law of Thermodynamics

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

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

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

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

Motion never stops at absolute zero!

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

Continued heating of a Solid Lattice

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

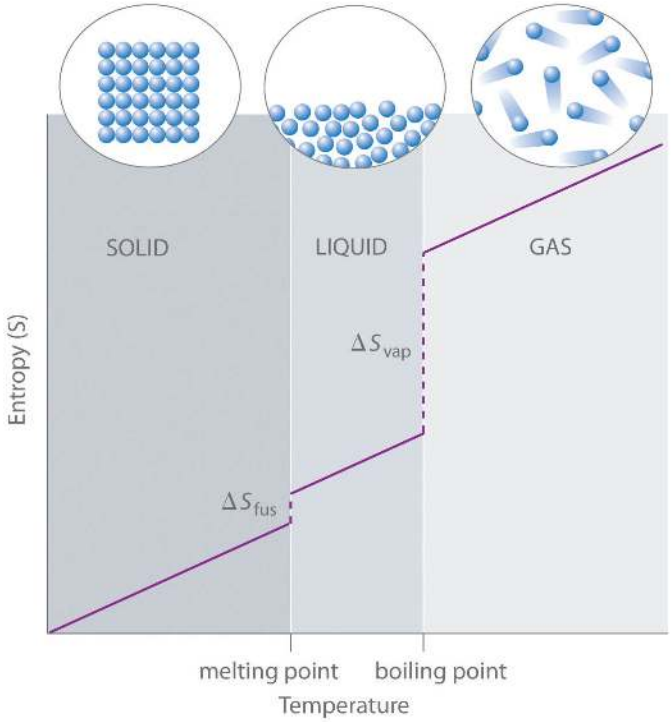


Figure **5.3.3**: A Generalized Plot of Entropy versus Temperature for a Single Substance. Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).

As shown in Table **5.3.1**, for substances with approximately the same molar mass and number of atoms, S° values fall in the order S°(gas) > S°(liquid) > S°(solid). For instance, S° for liquid water is 70.0 J/(mol·K), whereas S° for water vapor is 188.8 J/(mol·K). Likewise, S° is 260.7 J/(mol·K) for gaseous I_2 and 116.1 J/(mol·K) for solid I2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure **5.3.2**, which is a generalized plot of the entropy of a substance versus temperature.

Table **5.3.1**: Standard Molar Entropy Values of Selected Substances at 25°C

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

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

A closer examination of Table **5.3.1** also reveals that substances with similar molecular structures tend to have similar S° values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [S° = 2.4 J/(mol·K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher S° [5.7 J/(mol·K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the S° values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of S°, which reflects a more ordered structure.



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

Summary

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

1. The melting of a solid to form a liquid

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

Contributors and Attributions

- Mike Blaber (Florida State University)

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5.4: Gibbs Free Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for both a system and its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a system would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), often called simply free energy, was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{5.4.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the Amistad trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Chatelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The criterion for predicting spontaneity is based on (ΔG), the change in G, at constant temperature and pressure. Although very few chemical reactions actually occur under conditions of constant temperature and pressure, most systems can be brought back to the initial temperature and pressure without significantly affecting the value of thermodynamic state functions such as G. At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S \tag{5.4.2}$$

where all thermodynamic quantities are those of the system. Recall that at constant pressure, $\Delta H = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 5.4.2 to $\Delta G = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a system determines the direction in which change is spontaneous, we can rewrite the relationship between ΔS and q_{rev}, discussed earlier.

$$\Delta S = \frac{q_{rev}}{T} \tag{5.4.3}$$

with the definition of ΔH in terms of q_{rev}

$$q_{rev} = \Delta H \tag{5.4.4}$$

to obtain

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}}{T} \tag{5.4.5}$$

Thus the entropy change of the surroundings is related to the enthalpy change of the system. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \tag{5.4.6}$$

$$= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \tag{5.4.7}$$

Multiplying both sides of the inequality by −T reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{5.4.8}$$

which is equal to ΔG (Equation 5.4.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the surroundings and the heat gained or lost by the system provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 5.4.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H \ll 0$) that increase the disorder of a system ($\Delta S_{sys} \gg 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995. For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, $\Delta H = 40,657; J$, so the process is highly endothermic. From the definition of ΔS (Equation 5.4.5), we know that for 1 mol of water,

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{b}}} \\ &= \frac{40{,}657\ \text{J}}{373.15\ \text{K}} \\ &= 108.96\ \text{J/K}\end{aligned}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\begin{aligned}\Delta G_{100^\circ\text{C}} &= \Delta H_{100^\circ\text{C}} - T\Delta S_{100^\circ\text{C}} \\ &= 40{,}657\ \text{J} - [(373.15\ \text{K})(108.96\ \text{J/K})] \\ &= 0\ \text{J}\end{aligned}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions.

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\begin{aligned}\Delta G_{110^\circ\text{C}} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(383.15\ \text{K})(108.96\ \text{J/K})] \\ &= -1091\ \text{J}\end{aligned}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\begin{aligned}\Delta G_{90^\circ C} &= \Delta H - T\Delta S \\ &= 40{,}657\ \text{J} - [(363.15\ \text{K})(108.96\ \text{J/K})] \\ &= 1088\ \text{J}\end{aligned}$$

At 90°C, ΔG > 0, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110^\circ C} = 1090\ \text{J} = -\Delta G_{90^\circ C}$, as we would predict.

Relating Enthalpy and Entropy changes under Equilibrium Conditions

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 5.4.2), setting $\Delta G = 0$, and solving for T,

$$0\ \text{J} = 40{,}657\ \text{J} - T(108.96\ \text{J/K})$$
$$T = 373.15\ \text{K}$$

Thus $\Delta G = 0$ at T = 373.15 K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the normal boiling point of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 5.4.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

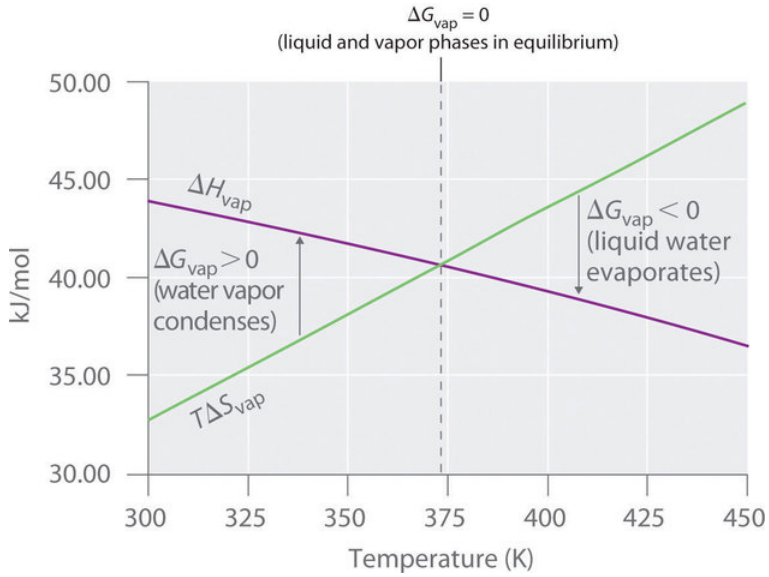


Figure 5.4.1: Temperature Dependence of ΔH and TΔS for the Vaporization of Water. Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy (ΔH > 0), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid (ΔS > 0). At temperatures greater than 373 K, the TΔS term dominates, and ΔG < 0, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 5.4.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{5.4.9}$$

This equation tells us that when energy is released during an exothermic process (ΔH < 0), such as during the combustion of a fuel, some of that energy can be used to do work (ΔG < 0), while some is used to increase the entropy of the universe (TΔS > 0). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see the previous section). Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 5.4.1, the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 5.4.1: Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach leaf cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10-20
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure changes in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their

standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 5.4.10:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5.4.10}$$

If ΔS° and ΔH° for a reaction have the same sign, then the sign of ΔG° depends on the relative magnitudes of the ΔH° and TΔS° terms. It is important to recognize that a positive value of ΔG° for a reaction does not mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

> A positive ΔG° means that the equilibrium constant is less than 1.

Example 5.4.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$H_2(g) + O_2(g) \rightleftharpoons H_2O_2(l)$$

At 25°C, the standard enthalpy change (ΔH°) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are:

- $S^\circ(H_2O_2)$ = 109.6 J/(mol•K),
- $S^\circ(O_2)$ = 205.2 J/(mol•K), and
- $S^\circ(H_2)$ = 130.7 J/(mol•K).

Is the reaction spontaneous as written?

Given: balanced chemical equation, ΔH° and S° for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A. Calculate ΔS° from the absolute molar entropy values given.
B. Use Equation 5.4.10, the calculated value of ΔS°, and other data given to calculate ΔG° for the reaction. Use the value of ΔG° to determine whether the reaction is spontaneous as written.

Solution

A To calculate ΔG° for the reaction, we need to know ΔH^o, ΔS^o, and T. We are given ΔH^o, and we know that T = 298.15 K. We can calculate ΔS° from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ &= S^\circ(H_2O_2) - [S^\circ(O_2) + S^\circ(H_2)] \\ &= [1\text{ mol } H_2O_2 \times 109.6\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}] + [1\text{ mol } O_2 \times 205.2\text{ J/(mol}\cdot\text{K)}]\} \\ &= -226.3\text{ J/K (per mole of } H_2O_2)\end{aligned}$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, ΔS^o is very negative for this reaction.

B Substituting the appropriate quantities into Equation 5.4.10,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -187.78\text{ kJ/mol} - (298.15\text{ K})[-226.3\text{ J/(mol}\cdot\text{K)} \times 1\text{ kJ/1000 J}] \\ &= -187.78\text{ kJ/mol} + 67.47\text{ kJ/mol} \\ &= -120.31\text{ kJ/mol}\end{aligned}$$

The negative value of ΔG^o indicates that the reaction is spontaneous as written. Because ΔS^o and ΔH^o for this reaction have the same sign, the sign of ΔG^o depends on the relative magnitudes of the ΔH^o and $T\Delta S^o$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable ΔS^o term and for the energy needed to break bonds in the reactants.

Exercise 5.4.1

Calculate the standard free-energy change (ΔG^o) at 25°C for the reaction

$$2H_2(g) + N_2(g) \rightleftharpoons N_2H_4(l).$$

Is the reaction spontaneous as written at 25°C?

Hint

At 25°C, the standard enthalpy change (ΔH^o) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are

- S°(N_2H_4) = 121.2 J/(mol•K),
- S°(N_2) = 191.6 J/(mol•K), and
- S°(H_2) = 130.7 J/(mol•K).

Answer

149.5 kJ/mol

no, not spontaneous

Video Solution

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG^o_f)of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^o_f = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation (ΔH°_f) and the standard entropy of formation (ΔS°_f) using the definition of free energy:

$$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f \tag{5.4.11}$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar “products minus reactants” rule:

$$\Delta G^o_{rxn} = \sum m\Delta G^o_f(products) - \sum n\Delta^o_f(reactants) \tag{5.4.12}$$

where m and n are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

The "Products minus Reactants" Rule

The ΔG^o of a reaction can be calculated from tabulated ΔG°_f values (Table T1) using the “products minus reactants” rule.

Example 5.4.2

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 7). Use the following data:

- ΔG°_f(isooctane) = −353.2 kJ/mol,
- $\Delta G^\circ_f(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^\circ_f(H_2O)$ = −237.1 kJ/mol. Is the reaction spontaneous as written?

Given: balanced chemical equation and values of ΔG°_f for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain ΔG°_{rxn}, remembering that ΔG°_f for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution

The balanced chemical equation for the reaction is as follows:

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

We are given ΔG°_f values for all the products and reactants except $O_2(g)$. Because oxygen gas is an element in its standard state, $\Delta G^\circ_f (O_2)$ is zero. Using the "products minus reactants" rule,

$$\begin{aligned}\Delta G^\circ &= [8\Delta G_f^\circ(CO_2) + 9\Delta G_f^\circ(H_2O)] - \left[1\Delta G_f^\circ(C_8H_{18}) + \frac{25}{2}\Delta G_f^\circ(O_2)\right] \\ &= [(8\text{ mol})(-394.4\text{ kJ/mol}) + (9\text{ mol})(-237.1\text{ kJ/mol})] \\ &\quad - \left[(1\text{ mol})(-353.2\text{ kJ/mol}) + \left(\frac{25}{2}\text{ mol}\right)(0\text{ kJ/mol})\right] \\ &= -4935.9\text{ kJ (per mol of } C_8H_{18})\end{aligned}$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

? Exercise 5.4.2

Calculate ΔG° for the reaction of benzene with hydrogen gas to give cyclohexane using the following data

- ΔG°_f(benzene) = 124.5 kJ/mol
- ΔG°_f (cyclohexane) = 217.3 kJ/mol.

Is the reaction spontaneous as written?

Answer

92.8 kJ; no

Video Solution

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and TΔS terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

✓ Example 5.4.3

Calculate (a) ΔG° and (b) $\Delta G_{300°C}$ for the reaction $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

- $S°(N_2)$ = 191.6 J/(mol•K),
- $S°(H_2)$ = 130.7 J/(mol•K),

- S°(NH_3) = 192.8 J/(mol•K), and
- ΔH°_f (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, S° values, and ΔH°_f for NH_3

Asked for: ΔG° and ΔG at 300°C

Strategy:

A. Convert each temperature to kelvins. Then calculate ΔS° for the reaction. Calculate ΔH° for the reaction, recalling that ΔH°_f for any element in its standard state is zero.
B. Substitute the appropriate values into Equation 5.4.10 to obtain ΔG° for the reaction.
C. Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 5.4.2 to obtain ΔG for the reaction at 300°C.

Solution

A To calculate ΔG° for the reaction using Equation 5.4.10, we must know the temperature as well as the values of ΔS° and ΔH°. At standard conditions, the temperature is 25°C, or 298 K. We can calculate ΔS° for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\begin{aligned}\Delta S^\circ_{rxn} &= 2S^\circ(NH_3) - [S^\circ(N_2) + 3S^\circ(H_2)] \\ &= [2\text{ mol } NH_3 \times 192.8\text{ J/(mol}\cdot\text{K)}] \\ &\quad - \{[1\text{ mol } N_2 \times 191.6\text{ J/(mol}\cdot\text{K)}] + [3\text{ mol } H_2 \times 130.7\text{ J/(mol}\cdot\text{K)}]\} \\ &= -198.1\text{ J/K (per mole of } N_2) \end{aligned} \tag{5.4.13}$$

We can also calculate ΔH° for the reaction using the "products minus reactants" rule. The value of ΔH°_f (NH_3) is given, and ΔH°_f is zero for both N_2 and H_2:

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\Delta H^\circ_f(NH_3) - [\Delta H^\circ_f(N_2) + 3\Delta H^\circ_f(H_2)] \\ &= [2 \times (-45.9\text{ kJ/mol})] - [(1 \times 0\text{ kJ/mol}) + (3 \times 0\text{ kJ/mol})] \\ &= -91.8\text{ kJ(per mole of } N_2)\end{aligned}$$

B Inserting the appropriate values into Equation 5.4.10

$$\begin{aligned}\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ &= (-91.8\text{ kJ}) - (298\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= -32.7\text{ kJ (per mole of } N_2)\end{aligned}$$

C To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300^\circ C}$ = H° and $\Delta S_{300^\circ C}$ = ΔS°) and insert the appropriate temperature (573 K) into Equation 5.4.2:

$$\begin{aligned}\Delta G_{300^\circ C} &= \Delta H_{300^\circ C} - (573\text{ K})(\Delta S_{300^\circ C}) \\ &= \Delta H^\circ - (573\text{ K})\Delta S^\circ \\ &= (-91.8\text{ kJ}) - (573\text{ K})(-198.1\text{ J/K})(1\text{ kJ}/1000\text{ J}) \\ &= 21.7\text{ kJ (per mole of } N_2)\end{aligned}$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the −TΔS° term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

? Exercise 5.4.3

Calculate

a. ΔG° and
b. $\Delta G_{750^\circ C}$

for the following reaction

$$2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

- S°(NO) = 210.8 J/(mol•K),
- S°(O_2) = 205.2 J/(mol•K),
- S°(NO_2) = 240.1 J/(mol•K),
- $\Delta H^\circ_f(NO_2)$ = 33.2 kJ/mol, and
- ΔH°_f (NO) = 91.3 kJ/mol.

Answer a

−72.5 kJ/mol of O_2

Answer b

33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both ΔH° and ΔS°. The temperature at which a given reaction is at equilibrium can be calculated by setting ΔG° = 0 in Equation 5.4.10, as illustrated in Example 5.4.4.

Example 5.4.4

As you saw in Example 5.4.3, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which ΔH° and ΔS° are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 9.5.3 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that ΔH° and ΔS° are independent of temperature.

Given: ΔH° and ΔS°

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set ΔG° equal to zero in Equation 5.4.10 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution

In Example 5.4.3, we calculated that ΔH° is −91.8 kJ/mol of N_2 and ΔS° is −198.1 J/K per mole of N_2, corresponding to ΔG° = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of ΔH° and ΔS°. The temperature at which the reaction becomes nonspontaneous is found by setting ΔG° equal to zero and rearranging Equation 5.4.10 to solve for T:

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

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

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{(-91.8\text{ kJ})(1000\text{ J/kJ})}{-198.1\text{ J/K}} = 463\text{ K}$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise 5.4.4

As you found in the exercise in Example 5.4.3, ΔH° and ΔS° are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer

792.6 K

Video Solution

Summary

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.
- Free-energy change:

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

- Standard free-energy change:

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

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called Gibbs free energy (G). The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, ΔG = 0. If the process is spontaneous, ΔG < 0. If the process is not spontaneous as written but is spontaneous in the reverse direction, ΔG > 0. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The standard free-energy change (ΔG°) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free energy of formation (ΔG°_f), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate ΔG° for a reaction.

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5.4.1: Gibbs Energy practice problems

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

Contributors

- Anonymous

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5.4.2: Free Energy and the Equilibrium Constant

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K.

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 5.4.2.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 5.4.2.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
Q < K	Q = K	Q > K
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG^o) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH^o and ΔS^o determine the magnitude and sign of ΔG^o and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG^o and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \tag{5.4.2.1}$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 5.4.2.1 simplifies to

$$\Delta G = V\Delta P \tag{5.4.2.2}$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 5.4.2.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively):

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P \tag{5.4.2.3}$$

$$= nRT\frac{\Delta P}{P} \tag{5.4.2.4}$$

$$= nRT\ln\left(\frac{P_f}{P_i}\right) \tag{5.4.2.5}$$

If the initial state is the standard state with $P_i = 1\ atm$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \tag{5.4.2.6}$$

As you will soon discover, Equation 5.4.2.6 allows us to relate ΔG^o and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD \tag{5.4.2.7}$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum_m G_{products} - \sum_n G_{reactants} \tag{5.4.2.8}$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \tag{5.4.2.9}$$

Substituting Equation 5.4.2.6 for each term into Equation 5.4.2.9,

$$\Delta G = [(cG^o_C + cRT \ln P_C) + (dG^o_D + dRT \ln P_D)] - [(aG^o_A + aRT \ln P_A) + (bG^o_B + bRT \ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) \tag{5.4.2.10}$$

$$= \Delta G^\circ + RT \ln Q \tag{5.4.2.11}$$

where ΔG^o indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG^o and K_p for gases as follows:

$$0 = \Delta G^o + RT \ln K_p \tag{5.4.2.12}$$

$$\Delta G^o = -RT \ln K_p \tag{5.4.2.13}$$

If the products and reactants are in their standard states and $\Delta G^o < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^o > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^o = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

> *For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.*

Example 5.4.2.1

ΔG^o is −32.7 kJ/mol of N_2 for the reaction

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

This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions:

- P_{N_2} = 2.00 atm,
- P_{H_2} = 7.00 atm,
- P_{NH_3} = 0.021 atm, and
- $T = 100^oC$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

A. Using the values given and Equation 5.4.2.11, calculate Q.
B. Determine if Q is >, <, or = to K
C. Substitute the values of ΔG^o and Q into Equation 5.4.2.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG^o and ΔG under nonstandard conditions is given in Equation 5.4.2.11. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}$$
$$= \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Because ΔG^o is −, K must be a number greater than 1

C Substituting the values of ΔG^o and Q into Equation 5.4.2.11,

$$\Delta G = \Delta G^\circ + RT \ln Q$$
$$= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \ln(6.4 \times 10^{-7})\right]$$
$$= -32.7 \text{ kJ} + (-44 \text{ kJ})$$
$$= -77 \text{ kJ/mol of } N_2$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 5.4.2.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, P_{NO} = 0.0100 atm, P_{O_2} = 0.200 atm, and $P_{NO_2} = 1.00 \times 10^{-4} atm$. The value of ΔG^o for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer

−92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

✔ Example 5.4.2.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. ΔG^o for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 5.4.2.1, ΔG^o, and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG^o and T (in kelvin) into Equation 5.4.2.13 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution

In Example 5.4.2.1, we used tabulated values of ΔG°_f to calculate ΔG^o for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 5.4.2.13,

$$\Delta G^\circ = -RT \ln K_\text{p}$$

$$\frac{-\Delta G^\circ}{RT} = \ln K_\text{p}$$

Inserting the value of ΔG^o and the temperature (25°C = 298 K) into this equation,

$$\ln K_\text{p} = -\frac{(-32.7\ \text{kJ})(1000\ \text{J/kJ})}{(8.314\ \text{J/K})(298\ \text{K})} = 13.2$$

$$K_\text{p} = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 5.4.2.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. ΔG^o for this reaction is −70.5 kJ/mol of O_2.

Answer

2.3×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \tag{5.4.2.14}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 5.4.2.13 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \tag{5.4.2.15}$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 5.4.2.15 for the difference between K_p and K.

Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 5.4.2.15 with $\Delta G^o = \Delta H^o - T\Delta S^o$ provides insight into how the components of ΔG^o influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5.4.2.16}$$

$$= -RT \ln K \tag{5.4.2.17}$$

Notice that K becomes larger as ΔS^o becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH^o decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

> *The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.*



Relating Grxn and Kp: Relating Grxn and Kp(opens in new window) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG^o and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 5.4.2.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{5.4.2.18}$$

Assuming ΔH^o and ΔS^o are temperature independent, for an exothermic reaction ($\Delta H^o < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction (ΔH° > 0), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 5.4.2.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 5.4.2.18 also shows that the magnitude of ΔH^o dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS^o affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH^o for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS^o. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 5.4.2.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5.4.2.19}$$

Thus calculating ΔH^o from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH^o and ΔS^o are independent of temperature.

Example 5.4.2.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 5.4.2.3. What is K_p at 500°C? (Use the data from Example 5.4.2.1.)

Given: balanced chemical equation, $\Delta H^{\circ\circ}$, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 5.4.2.19 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of ΔH^o for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 5.4.2.19 we obtain the following:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{(-91.8\ \text{kJ})(1000\ \text{J/kJ})}{8.314\ \text{J/K}}\left(\frac{1}{298\ \text{K}} - \frac{1}{773\ \text{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \times 10^{-10}$$

$$K_2 = (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

? Exercise 5.4.2.4

In the exercise in Example **5.4.2.3**, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the ΔH_f^o values in the exercise in Example **5.4.2.1** to calculate K_p for this reaction at 1000°C.

Answer

5.6×10^{-4}



The Van't Hoff Equation: The Van't Hoff Equation (opens in new window) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G^o < 0$, then K > 1, and products are favored over reactants at equilibrium. Conversely, if $\Delta G^o > 0$, then K < 1, and reactants are favored over products at equilibrium. If

ΔG^o = 0, then K=1, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

- Mike Blaber (Florida State University)
- Modified by Tom Neils (Grand Rapids Community College)

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5.5: Photosynthesis

The adjective *fossil* describes the fossil fuels very aptly, because all of them are derived from the remains of plants or animals which lived on earth millions of years ago. Coal, for example, began as plant matter in prehistoric swamps, where it was able to decompose in the absence of air. Present-day peat bogs are examples of this first stage in coal formation, and in countries such as Ireland dried peat is an important fuel. Over long periods of time, at high temperatures and pressures under the earth's surface, peat can be transformed into lignite, a brown, soft form of coal. Continued action of geological forces converts lignite into bituminous, or soft coal, and eventually into anthracite, or hard coal. When burned, these latter two types of coal release considerably more heat per unit mass than do lignite or peat.

A crucial point to realize about fossil fuels is that the energy we release by burning them came originally from the sun. The plants from which the fuels were derived grew as a result of **photosynthesis**, the combination of carbon dioxide and water under the influence of sunlight to form organic compounds whose empirical formula is approximately

$$\mathrm{CO_2\,(g) + H_2O\,(l) \rightarrow [CH_2O]\,(s) + O_2\,(g)} \tag{5.5.1}$$

with $\Delta H \approx 469\,\mathrm{kJ\ mol^{-1}}$

Since a number of different substances are formed by photosynthesis, the empirical formula $[CH_2O]$ and the ΔH are only approximate.

Photosynthesis is endothermic, and the necessary energy is supplied by the absorption of solar radiant energy. This energy can be released by carrying out the reverse of Equation 5.5.1, a process which is exothermic. When we burn paper, wood, or dried leaves, the heat given off is really a stored form of sunlight. Plants and animals obtain the energy they need to grow or move about from the oxidation of substances produced by photosynthesis. This oxidation process is called respiration.

After millions of years of geological change, the fossil fuels are significantly different in chemical structure from newly photosynthesized plant or animal material. The changes which occur can be approximated by the equation for formation of methane (natural gas):

$$\mathrm{2\,[CH_2O] \rightarrow CH_4\,(g) + CO_2\,(g)}$$

with $\Delta H \approx -47\,\mathrm{kJ\ mol^{-1}}$.

This reaction is only slightly exothermic, and so very little of the energy captured from sunlight is lost. However, about half the carbon and all the oxygen are lost as carbon dioxide gas, and so a fossil fuel like methane can release more heat per carbon atom (and per gram) than can wood or other organic materials. This is why anthracite and bituminous coals are better fuels than the peat from which they are formed. The enthalpy changes which occur during photosynthesis, respiration, and formation and combustion of fossil fuels are summarized in Figure 5.5.1.

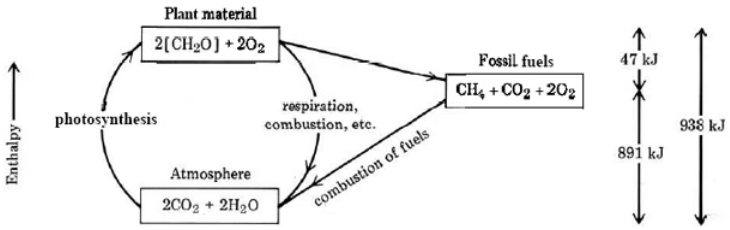


Figure 5.5.1: Diagram to show enthalpy relationships of the atmosphere, plant materials, and the fossil fuels.

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5.E: Chemical Thermodynamics (Practice Problems with Answers)

19.1: Spontaneous Processes

19.2: Entropy and the Second Law of Thermodynamics

Conceptual Problems

1. A Russian space vehicle developed a leak, which resulted in an internal pressure drop from 1 atm to 0.85 atm. Is this an example of a reversible expansion? Has work been done?
2. Which member of each pair do you expect to have a higher entropy? Why?

    a. solid phenol or liquid phenol
    b. 1-butanol or butane
    c. cyclohexane or cyclohexanol
    d. 1 mol of N_2 mixed with 2 mol of O_2 or 2 mol of NO_2
    e. 1 mol of O_2 or 1 mol of O_3
    f. 1 mol of propane at 1 atm or 1 mol of propane at 2 atm

3. Determine whether each process is reversible or irreversible.

    a. ice melting at 0°C
    b. salt crystallizing from a saline solution
    c. evaporation of a liquid in equilibrium with its vapor in a sealed flask
    d. a neutralization reaction

4. Determine whether each process is reversible or irreversible.

    a. cooking spaghetti
    b. the reaction between sodium metal and water
    c. oxygen uptake by hemoglobin
    d. evaporation of water at its boiling point

5. Explain why increasing the temperature of a gas increases its entropy. What effect does this have on the internal energy of the gas?
6. For a series of related compounds, does ΔS_{vap} increase or decrease with an increase in the strength of intermolecular interactions in the liquid state? Why?
7. Is the change in the enthalpy of reaction or the change in entropy of reaction more sensitive to changes in temperature? Explain your reasoning.
8. Solid potassium chloride has a highly ordered lattice structure. Do you expect ΔS_{soln} to be greater or less than zero? Why? What opposing factors must be considered in making your prediction?
9. Aniline ($C_6H_5NH_2$) is an oily liquid at 25°C that darkens on exposure to air and light. It is used in dying fabrics and in staining wood black. One gram of aniline dissolves in 28.6 mL of water, but aniline is completely miscible with ethanol. Do you expect ΔS_{soln} in H_2O to be greater than, less than, or equal to ΔS_{soln} in CH_3CH_2OH? Why?

Conceptual Answers

1. No, it is irreversible; no work is done because the external pressure is effectively zero.
3.

    a. reversible
    b. irreversible
    c. reversible
    d. irreversible

9. Water has a highly ordered, hydrogen-bonded structure that must reorganize to accommodate hydrophobic solutes like aniline. In contrast, we expect that aniline will be able to disperse randomly throughout ethanol, which has a significantly less ordered structure. We therefore predict that ΔS_{soln} in ethanol will be more positive than ΔS_{soln} in water.

Numerical Problems

1. Liquid nitrogen, which has a boiling point of −195.79°C, is used as a coolant and as a preservative for biological tissues. Is the entropy of nitrogen higher or lower at −200°C than at −190°C? Explain your answer. Liquid nitrogen freezes to a white solid at −210.00°C, with an enthalpy of fusion of 0.71 kJ/mol. What is its entropy of fusion? Is freezing biological tissue in liquid nitrogen an example of a reversible process or an irreversible process?
2. Using the second law of thermodynamics, explain why heat flows from a hot body to a cold body but not from a cold body to a hot body.
3. One test of the spontaneity of a reaction is whether the entropy of the universe increases: $\Delta S_{univ} > 0$. Using an entropic argument, show that the following reaction is spontaneous at 25°C:

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

   Why does the entropy of the universe increase in this reaction even though gaseous molecules, which have a high entropy, are consumed?

4. Calculate the missing data in the following table.

Compound	ΔH_{fus} (kJ/mol)	ΔS_{fus} [J/(mol·K)]	Melting Point (°C)
acetic acid	11.7		16.6
CH_3CN	8.2	35.9	
CH_4	0.94		−182.5
CH_3OH		18.2	−97.7
formic acid	12.7	45.1	

   Based on this table, can you conclude that entropy is related to the nature of functional groups? Explain your reasoning.

5. Calculate the missing data in the following table.

Compound	ΔH_{vap} (kJ/mol)	ΔS_{vap} [J/(mol·K)]	Boiling Point (°C)
hexanoic acid	71.1		105.7
hexane	28.9	85.5	
formic acid		60.7	100.8
1-hexanol	44.5		157.5

   The text states that the magnitude of ΔS_{vap} tends to be similar for a wide variety of compounds. Based on the values in the table, do you agree?

19.3: The Molecular Interpretation of Entropy

19.4: Entropy Changes in Chemical Reactions

19.5: Gibbs Free Energy

Conceptual Problems

1. How does each example illustrate the fact that no process is 100% efficient?

a. burning a log to stay warm
b. the respiration of glucose to provide energy
c. burning a candle to provide light

2. Neither the change in enthalpy nor the change in entropy is, by itself, sufficient to determine whether a reaction will occur spontaneously. Why?
3. If a system is at equilibrium, what must be the relationship between ΔH and ΔS?
4. The equilibrium $2AB \rightleftharpoons A_2B_2$ is exothermic in the forward direction. Which has the higher entropy—the products or the reactants? Why? Which is favored at high temperatures?
5. Is ΔG a state function that describes a system or its surroundings? Do its components—ΔH and ΔS—describe a system or its surroundings?
6. How can you use ΔG to determine the temperature of a phase transition, such as the boiling point of a liquid or the melting point of a solid?
7. Occasionally, an inventor claims to have invented a “perpetual motion” machine, which requires no additional input of energy once the machine has been put into motion. Using your knowledge of thermodynamics, how would you respond to such a claim? Justify your arguments.
8. Must the entropy of the universe increase in a spontaneous process? If not, why is no process 100% efficient?
9. The reaction of methyl chloride with water produces methanol and hydrogen chloride gas at room temperature, despite the fact that $\Delta H^\circ_{rxn} = 7.3$ kcal/mol. Using thermodynamic arguments, propose an explanation as to why methanol forms.

Conceptual Answers

9. In order for the reaction to occur spontaneously, ΔG for the reaction must be less than zero. In this case, ΔS must be positive, and the $T\Delta S$ term outweighs the positive value of ΔH.

Numerical Problems

1. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

a. $\mathbf{H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)}$
b. $2H_2(g) + C_2H_2(g) \rightarrow C_2H_6(g)$
c. $(CH_3)_2O(g) + H_2O(g) \rightarrow 2CH_3OH(l)$
d. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

2. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.

a. $K_2O_2(s) \rightarrow 2K(s) + O_2(g)$
b. $PbCO_3(s) \rightarrow PbO(s) + CO_2(g)$
c. $P_4(s) + 6H_2(g) \rightarrow 4PH_3(g)$
d. $2AgCl(s) + H_2S(g) \rightarrow Ag_2S(s) + 2HCl(g)$

3. Nitrogen fixation is the process by which nitrogen in the atmosphere is reduced to NH_3 for use by organisms. Several reactions are associated with this process; three are listed in the following table. Which of these are spontaneous at 25°C? If a reaction is not spontaneous, at what temperature does it become spontaneous?

Reaction	ΔH°_{298} (kcal/mol)	ΔS°_{298} [cal/(°·mol)]
(a) $\mathbf{\frac{1}{2}N_2 + O_2 \rightarrow NO_2}$	8.0	−14.4
(b) $\mathbf{\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO}$	21.6	2.9
(c) $\mathbf{\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3}$	−11.0	−23.7

4. A student was asked to propose three reactions for the oxidation of carbon or a carbon compound to CO or CO_2. The reactions are listed in the following table. Are any of these reactions spontaneous at 25°C? If a reaction does not occur spontaneously at 25°C, at what temperature does it become spontaneous?

Reaction	ΔH°_{298} (kcal/mol)	ΔS°_{298} [cal/(°·mol)]
$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	42	32
$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$	−9.8	−10.1
$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$	49.3	51.3

5. Tungsten trioxide (WO_3) is a dense yellow powder that, because of its bright color, is used as a pigment in oil paints and water colors (although cadmium yellow is more commonly used in artists' paints). Tungsten metal can be isolated by the reaction of WO_3 with H_2 at 1100°C according to the equation $WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$. What is the lowest temperature at which the reaction occurs spontaneously? $\Delta H° = 27.4$ kJ/mol and $\Delta S° = 29.8$ J/K.

6. Sulfur trioxide (SO_3) is produced in large quantities in the industrial synthesis of sulfuric acid. Sulfur dioxide is converted to sulfur trioxide by reaction with oxygen gas.

    a. Write a balanced chemical equation for the reaction of SO_2 with $O_2(g)$ and determine its $\Delta G°$.
    b. What is the value of the equilibrium constant at 600°C?
    c. If you had to rely on the equilibrium concentrations alone, would you obtain a higher yield of product at 400°C or at 600°C?

7. Calculate $\Delta G°$ for the general reaction $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ at 25°C, where M is Mg or Ba. At what temperature does each of these reactions become spontaneous?

Compound	ΔH°_f (kJ/mol)	S° [J/(mol·K)]
MCO_3		
Mg	−1111	65.85
Ba	−1213.0	112.1
MO		
Mg	−601.6	27.0
Ba	−548.0	72.1
CO_2	−393.5	213.8

8. The reaction of aqueous solutions of barium nitrate with sodium iodide is described by the following equation:

$$Ba(NO_3)_2(aq) + 2NaI(aq) \rightarrow BaI_2(aq) + 2NaNO_3(aq)$$

You want to determine the absolute entropy of BaI_2, but that information is not listed in your tables. However, you have been able to obtain the following information:

	$Ba(NO_3)_2$	NaI	BaI_2	$NaNO_3$
ΔH°_f (kJ/mol)	−952.36	−295.31	−605.4	−447.5
S° [J/(mol·K)]	302.5	170.3		205.4

You know that $\Delta G°$ for the reaction at 25°C is 22.64 kJ/mol. What is $\Delta H°$ for this reaction? What is S° for BaI_2?

Numerical Answers

1.

a. −237.1 kJ/mol; spontaneous as written
b. −241.9 kJ/mol; spontaneous as written
c. 8.0 kJ/mol; spontaneous in reverse direction.
d. 141.9 kJ/mol; spontaneous in reverse direction.

3.

a. Not spontaneous at any T
b. Not spontaneous at 25°C; spontaneous above 7400 K
c. Spontaneous at 25°C

5. 919 K

7. $MgCO_3$: $\Delta G° = 63$ kJ/mol, spontaneous above 663 K; $BaCO_3$: $\Delta G° = 220$ kJ/mol, spontaneous above 1562 K

19.6: Free Energy and Temperature

19.7: Free Energy and the Equilibrium Constant

Conceptual Problems

1. Do you expect products or reactants to dominate at equilibrium in a reaction for which $\Delta G°$ is equal to

a. 1.4 kJ/mol?
b. 105 kJ/mol?
c. −34 kJ/mol?

2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?

3. What happens to the change in free energy of the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$ if the pressure is increased while the temperature remains constant? if the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?

4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

Numerical Problems

1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form CO_2 and H_2, as shown in the equation $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$, for which $\Delta H° = -41.0$ kJ/mol and $\Delta S° = -42.3$ J cal/(mol·K) at 25°C and 1 atm.

a. What is $\Delta G°$ for this reaction?
b. What is ΔG if the gases have the following partial pressures: $P_{CO} = 1.3$ atm, $P_{H_2O} = 0.8$ atm, $P_{CO_2} = 2.0$ atm, and $P_{H_2} = 1.3$ atm?
c. What is ΔG if the temperature is increased to 150°C assuming no change in pressure?

2. Methane and water react to form carbon monoxide and hydrogen according to the equation $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$.

a. What is the standard free energy change for this reaction?
b. What is K_p for this reaction?
c. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?
d. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?
e. At what temperature does the reaction become spontaneous?

3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

    a. $CCl_4(g)+6H_2O(l)\rightleftharpoons CO_2(g)+4HCl(aq)$; $\Delta G° = -377$ kJ/mol
    b. $Xe(g)+2F_2(g)\rightleftharpoons XeF_4(s)$; $\Delta H° = -66.3$ kJ/mol, $\Delta S° = -102.3$ J/(mol·K)
    c. $PCl_3(g)+S\rightleftharpoons PSCl_3(l)$; $\Delta G^\circ_f(PCl_3) = -272.4$ kJ/mol, $\Delta G^\circ_f(PSCl_3) = -363.2$ kJ/mol

4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.

    a. $2KClO_3(s)\rightleftharpoons 2KCl(s)+3O_2(g)$; $\Delta G° = -225.8$ kJ/mol
    b. $CoCl_2(s)+6H_2O(g)\rightleftharpoons CoCl_2\cdot 6H_2O(s)$; $\Delta H^\circ_{rxn} = -352$ kJ/mol, $\Delta S^\circ_{rxn} = -899$ J/(mol·K)
    c. $2PCl_3(g)+O_2(g)\rightleftharpoons 2POCl_3(g)$; $\Delta G^\circ_f(PCl_3) = -272.4$ kJ/mol, $\Delta G^\circ_f(POCl_3) = -558.5$ kJ/mol

5. The gas-phase decomposition of N_2O_4 to NO_2 is an equilibrium reaction with $K_p = 4.66 \times 10^{-3}$. Calculate the standard free-energy change for the equilibrium reaction between N_2O_4 and NO_2.

6. The standard free-energy change for the dissolution $K_4Fe(CN)_6\cdot H_2O(s)\rightleftharpoons 4K^+(aq)+Fe(CN)_6^{4-}(aq)+H_2O(l)$ is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?

7. Ammonia reacts with water in liquid ammonia solution (am) according to the equation $NH_3(g) + H_2O(am) \rightleftharpoons NH_4^+(am) + OH^-(am)$. The change in enthalpy for this reaction is 21 kJ/mol, and $\Delta S° = -303$ J/(mol·K). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (−31°C)?

8. At 25°C, a saturated solution of barium carbonate is found to have a concentration of $[Ba^{2+}] = [CO_3^{2-}] = 5.08 \times 10^{-5}$ M. Determine $\Delta G°$ for the dissolution of $BaCO_3$.

9. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions is $Pb_3(PO_4)_2(s)+4H^+(aq)\rightleftharpoons 3Pb^{2+}(aq)+2H_2PO_4^-(aq)$, for which $\log K = -1.80$. What is $\Delta G°$ for this reaction?

10. The conversion of butane to 2-methylpropane is an equilibrium process with $\Delta H° = -2.05$ kcal/mol and $\Delta G° = -0.89$ kcal/mol.

    a. What is the change in entropy for this conversion?
    b. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?
    c. What is the equilibrium constant for this reaction?

11. The reaction of $CaCO_3(s)$ to produce $CaO(s)$ and $CO_2(g)$ has an equilibrium constant at 25°C of 2×10^{-23}. Values of ΔH°_f are as follows: $CaCO_3$, −1207.6 kJ/mol; CaO, −634.9 kJ/mol; and CO_2, −393.5 kJ/mol.

    a. What is $\Delta G°$ for this reaction?
    b. What is the equilibrium constant at 900°C?
    c. What is the partial pressure of $CO_2(g)$ in equilibrium with CaO and $CaCO_3$ at this temperature?
    d. Are reactants or products favored at the lower temperature? at the higher temperature?

12. In acidic soils, dissolved Al^{3+} undergoes a complex formation reaction with SO_4^{2-} to form $[AlSO_4^+]$. The equilibrium constant at 25°C for the reaction $Al^{3+}(aq)+SO_4^{2-}(aq)\rightleftharpoons AlSO_4^+(aq)$ is 1585.

    a. What is $\Delta G°$ for this reaction?
    b. How does this value compare with $\Delta G°$ for the reaction $Al^{3+}(aq)+F^-(aq)\rightleftharpoons AlF^{2+}(aq)$, for which $K = 10^7$ at 25°C?
    c. Which is the better ligand to use to trap Al^{3+} from the soil?

Numerical Answers

1.

    a. −28.4 kJ/mol
    b. −26.1 kJ/mol
    c. −19.9 kJ/mol

3.

    a. 1.21×10^{66}; equilibrium lies far to the right.
    b. 1.89×10^6; equilibrium lies to the right.

c. 5.28×10^{16}; equilibrium lies far to the right.

5. 13.3 kJ/mol

7. 5.1×10^{-21}

9. 10.3 kJ/mol

11.

a. 129.5 kJ/mol
b. 6
c. 6.0 atm
d. Products are favored at high T; reactants are favored at low T.

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CHAPTER OVERVIEW

6: Electrochemistry

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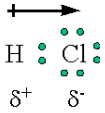
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6.1: Oxidation and Reduction Review

Electron transfer is one of the most basic processes that can happen in chemistry. It simply involves the movement of an electron from one atom to another. Many important biological processes rely on electron transfer, as do key industrial transformations used to make valuable products. In biology, for example, electron transfer plays a central role in respiration and the harvesting of energy from glucose, as well as the storage of energy during photosynthesis. In society, electron transfer has been used to obtain metals from ores since the dawn of civilization.

Oxidation States (Numbers)

Oxidation state is a useful tool for keeping track of electron transfers. It is most commonly used in dealing with metals and especially with transition metals. Unlike metals from the first two columns of the periodic table, such as sodium or magnesium, transition metals can often transfer different numbers of electrons, leading to different metal ions (e.g., sodium is generally found as Na^+ and magnesium is almost always Mg^{2+}, but manganese could be Mn^{2+}, Mn^{3+}, and so on, as far as Mn^{7+}). Oxidation state is a number assigned to an element in a compound according to some rules. This number enables us to describe oxidation-reduction reactions, and balancing redox chemical reactions. When a covalent bond forms between two atoms with different electronegativities the shared electrons in the bond lie closer to the more electronegative atom:



For hydrochloric acid, the hydrogen is positive while the chlorine is negative. The dipole starts at the hydrogen and points towards the chlorine.

The **oxidation state** of an atom is the charge that results when the electrons in a covalent bond are assigned to the more electronegative atom and is the charge an atom would possess *if the bonding were ionic*. In HCl (above) the oxidation number for the hydrogen would be +1 and that of the Cl would be -1.

Example 6.1.1

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the Oxidation State of each):

a. $Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$
b. $2\,Al + 3\,Cu^{2+} \longrightarrow 2\,Al^{3+} + 3\,Cu$
c. $CO_3^{2-} + 2\,H^+ \longrightarrow CO_2 + H_2O$

Solutions

a. Zn is oxidized (Oxidation number: 0 → +2); H^+ is reduced (Oxidation number: +1 → 0)
b. Al is oxidized (Oxidation number: 0 → +3); Cu^{2+} is reduced (+2 → 0)
c. This is not a redox reaction because each element has the same oxidation number in both reactants and products: O= -2, H= +1, C= +4.

An atom is oxidized if its oxidation number increases, and an atom is reduced if its oxidation number decreases. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation Numbers and Nomenclature

Compounds of the alkali (oxidation number +1) and alkaline earth metals (oxidation number +2) are typically ionic in nature. Compounds of metals with higher oxidation numbers (e.g., tin +4) tend to form molecular compounds

- In ionic and covalent molecular compounds usually the ***less electronegative element is given first***.
- In ionic compounds the names are given which refer to ***the oxidation (ionic) state***
- In molecular compounds the names are given which refer ***to the number of molecules present in the compound***

Figure **6.1.1**: Example of nomenclature based on oxidation states.

Ionic		Molecular	
MgH_2	magnesium hydride	H_2S	dihydrogen sulfide
FeF_2	iron(II) fluoride	OF_2	oxygen difluoride
Mn_2O_3	manganese(III) oxide	Cl_2O_3	dichlorine trioxide

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

Oxidation-Reduction Reaction Examples

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG,** meaning "*oxidation is loss*" and "*reduction is gain*," and **LEO says GER,** meaning "*loss of* e^- *= oxidation*" and "*gain of* e^- *= reduced*." There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons is called the **oxidizing agent**; by accepting electrons it causes the oxidation of another species. Conversely, the species that donates electrons is called the **reducing agent**; when the reaction occurs, it reduces the other species. In other words, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions).



Figure **6.1.1**: A thermite reaction taking place on a cast iron skillet. A thermite reaction, using about 110 g of the mixture, taking place. The cast-iron skillet was destroyed in the process. (CC BY-SA 2.5 generic; Schuyler S via Wikipedia).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) **O** atoms to **Al** atoms, producing $\mathbf{Al_2O_3}$ (Figure **6.1.1**).

$$\mathbf{Fe_2O_3\,(s) + 2\,Al\,(s) \longrightarrow Al_2O_3\,(s) + 2\,Fe\,(l)}$$

Another example of the redox reaction (although less dangerous) is the reaction between zinc and copper sulfate.

$$\mathbf{Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu}$$

Example 6.1.2: Identifying Oxidized and Reduced Elements

Determine what is oxidized and what is reduced in the following reaction.

$$\mathbf{Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2}$$

Solution

The oxidation state of H^+ changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the reducing agent.

The oxidation state of H^+ changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, H^+ ion is reduced and acts as the oxidizing agent.

Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given below:

$$A + B \rightarrow AB$$

Example 6.1.3: Combination Reaction

Equation:

$$H_2 + O_2 \longrightarrow H_2O$$

Calculation: 0 + 0 → **(2)(+1) + (-2) = 0**

Explanation:

In this equation both H_2 and O_2 are free elements; following Rule #1, their Oxidation States are 0. The product is H_2O, which has a total Oxidation State of 0. According to Rule #6, the Oxidation State of oxygen is usually -2. Therefore, the Oxidation State of H in H_2O must be +1.

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:

$$AB \rightarrow A + B$$

Example 6.1.4: Decomposition Reaction

Identify the oxidation state of the products and reactant in the decomposition of water:

$$H_2O \rightarrow H_2 + O_2$$

Calculation

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

In this reaction, water is "decomposed" into hydrogen and oxygen. As in the previous example the H_2O has a total Oxidation State of 0; thus, according to Rule #6 the Oxidation State of oxygen is usually -2, so the Oxidation State of hydrogen in H_2O must be +1.

Single Replacement Reactions

A single replacement reaction involves the "replacing" of an element in the reactants with another element in the products:

\[\ce{A + BC \rightarrow AB + C} \nonumber \]

Example 6.1.5: Single Replacement Reaction

Chlorine gas is a great oxidizing agent and will replace bromide ions from sodium bromide salt.

$$Cl_2(g) + Na\ \underline{Br}(s) \longrightarrow Na\underline{Cl}(s) + Br_2(l)$$

Explanation

In this equation, **Br** is replaced with **Cl**, and the **Cl** atoms in Cl_2 are reduced, while the **Br** ion in **NaBr** is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a single replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

\[\ce{AB + CD \rightarrow AD + CB} \nonumber \]

Example 6.1.6: Double Replacement Reaction

The reaction of gaseous hydrogen chloride and iron oxide is a double replacement reaction. Write the expected reaction for this chemistry equation.

Solution

$$Fe_2O_3 + 6\,HCl \longrightarrow 2\,FeCl_3 + 3\,H_2O$$

In this equation, **Fe** and **H** trade places, and oxygen and chlorine trade places.

Combustion Reactions

Combustion reactions almost always involve oxygen in the form of O_2, and are almost always exothermic, meaning they produce heat. Chemical reactions that give off light and heat and light are colloquially referred to as "burning."

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals "burn" in other environments. For example, both titanium and magnesium burn in nitrogen as well:

$$2\,Ti\,(s) + N_2\,(g) \longrightarrow 2\,TiN\,(s)$$

$$3\,Mg\,(s) + N_2\,(g) \longrightarrow Mg_3N_2\,(s)$$

Moreover, chemicals can be oxidized by other chemicals than oxygen, such as Cl_2 or F_2; these processes are also considered combustion reactions

Disproportionation Reactions

A single substance can be both oxidized and reduced in some redox reactions. These are known as **disproportionation reactions**, with the following general equation:

$$2\,A \longrightarrow A^{+n} + A^{-n}$$

where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

Example 6.1.7: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, H_2O_2 poured over a cut. This is a decomposition reaction of hydrogen peroxide (catalyzed by the catalase enzyme) that produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:

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

Explanation

On the reactant side, **H** has an Oxidation State of +1 and **O** has an Oxidation State of -1, which changes to -2 for the product H_2O (oxygen is reduced), and 0 in the product O_2 (oxygen is oxidized).



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

Summary

Oxidation signifies a loss of electrons and reduction signifies a gain of electrons. Balancing redox reactions is an important step that changes in neutral, basic, and acidic solutions. The types of redox reactions: Combination and decomposition, Displacement reactions (single and double), Combustion, Disproportionation. The oxidizing agent undergoes reduction and the reducing agent undergoes oxidation.

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Contributors and Attributions

- Christopher Spohrer (UCD), Christina Breitenbuecher (UCD), Luvleen Brar (UCD)
- Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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6.2: Balancing Oxidation-Reduction Equations

Learning Objectives

- To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of $Cr^{2+}(aq)$ with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 6.2.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\overset{+2}{Cr^{2+}}(aq) + \overset{+4}{Mn}\overset{-2}{O_2}(aq) + \overset{+1}{H^+}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq) + \overset{+2}{Mn^{2+}}(aq) + \overset{+1}{H_2}\overset{-2}{O}(l) \tag{6.2.1}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$Cr^{2+} + Mn^{4+} \longrightarrow Cr^{3+} + Mn^{2+} \tag{6.2.2}$$

The oxidation can be written as

$$\underbrace{Cr^{2+} \longrightarrow Cr^{3+} + e^-}_{\text{oxidation with 1 electron lost}} \tag{6.2.3}$$

and the reduction as

$$\underbrace{Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}}_{\text{reduction with 2 electrons gained}} \tag{6.2.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 6.2.3) by 2 to give

$$2\,Cr^{2+} \longrightarrow 2\,Cr^{3+} + 2\,e^- \tag{6.2.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 6.2.4):

$$2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + 2\,e^-$$

$$Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + \cancel{2e^-}$$

$$Mn^{4+} + \cancel{2e^-} \rightarrow Mn^{2+}$$

to result in the balanced redox reaction (metals only)

$$\mathrm{Mn^{4+} + 2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + Mn^{2+}} \tag{6.2.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$\mathrm{MnO_2\,(aq) + 2\,Cr^{2+}\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq)} \tag{6.2.7}$$

> *In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 6.2.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add $\mathrm{H^+}$ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding $\mathrm{OH^-}$ as necessary to either side of the equation to balance the charges.

In this case, adding four $\mathrm{H^+}$ ions to the left side of Equation 6.2.7 to give

$$\mathrm{MnO_2\,(s) + 2\,Cr^{2+}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq)} \tag{6.2.8}$$

Although the charges are now balanced in Equation 6.2.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding $\mathrm{H_2O}$ as necessary to either side of the equation. Here, we need to add two $\mathrm{H_2O}$ molecules to the right side of Equation 6.2.8:

$$\mathrm{MnO_2\,(s) + 2\,Cr^{2+}\,(aq) + 4\,H^+\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + Mn^{2+}\,(aq) + 2\,H_2O\,(l)} \tag{6.2.9}$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example 6.2.1 below.

Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding $\mathrm{H_2O}$ molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

Example 6.2.1: Balancing in Acid Solutions

Arsenic acid ($\mathrm{H_3AsO_4}$) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine ($\mathrm{AsH_3}$, a highly toxic and unstable gas) and $\mathrm{Zn^{2+}\,(aq)}$. Balance the equation for this reaction using oxidation states:

$$\mathrm{H_3AsO_4\,(aq) + Zn\,(s) \longrightarrow AsH_3\,(g) + Zn^{2+}\,(aq)}$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. *Write a chemical equation showing the reactants and the products.* Because we are given this information, we can skip this step.
2. *Assign oxidation states and determine which atoms change oxidation state.* The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$\overset{+5}{H_3As}O_4(aq) + \overset{0}{Zn}(s) \rightarrow \overset{-3}{As}H_3(g) + \overset{+2}{Zn^{2+}}(aq)$$

3. *Write separate equations for oxidation and reduction.* The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\underbrace{\overset{+5}{As} + 8e^- \rightarrow \overset{-3}{As}}_{\text{Reduction with gain of 8 electrons}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\underbrace{\overset{0}{Zn} \rightarrow \overset{+2}{Zn^{2+}} + 2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. *Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.* The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\begin{aligned} \overset{+5}{\text{As}} + 8\,\text{e}^- &\rightarrow \overset{-3}{\text{As}} \\ 4\,\overset{0}{\text{Zn}} &\rightarrow 4\,\overset{+2}{\text{Zn}^{2+}} + 8\,\text{e}^- \end{aligned}$$

5. *Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.* Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives
   - Reduction:

$$\text{H}_3\text{AsO}_4\,(\text{aq}) + 8\,\text{e}^- \rightarrow \text{AsH}_3\,(\text{g})$$

   - Oxidation:

$$4\,\text{Zn}\,(\text{s}) \longrightarrow 4\,\text{Zn}^{2+}\,(\text{aq}) + 8\,\text{e}^-$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$\text{H}_3\text{AsO}_4\,(\text{aq}) + 4\,\text{Zn}\,(\text{s}) + \cancel{8\text{e}^-} \rightarrow \text{AsH}_3\,(\text{g}) + 4\,\text{Zn}^{2+}\,(\text{aq}) + \cancel{8\text{e}^-}$$

which then yields after canceling electrons

$$\text{H}_3\text{AsO}_4\,(\text{aq}) + 4\,\text{Zn}\,(\text{s}) \rightarrow \text{AsH}_3\,(\text{g}) + 4\,\text{Zn}^{2+}\,(\text{aq})$$

7. *Balance the charge by adding* H^+ *or* OH^- *ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$\text{H}_3\text{AsO}_4\,(\text{aq}) + 4\,\text{Zn}\,(\text{s}) + 8\,\text{H}^+\,(\text{aq}) \rightarrow \text{AsH}_3\,(\text{g}) + 4\,\text{Zn}^{2+}\,(\text{aq})$$

8. *Balance the oxygen atoms by adding H_2O molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 H_2O molecules to the right side balances the O atoms:

$$H_3AsO_4(aq) + 4\,Zn(s) + 8\,H^+(aq) \rightarrow AsH_3(g) + 4\,Zn^{2+}(aq) + 4\,H_2O(l)$$

Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
   - Atoms:

$$1\,As + 4\,Zn + 4\,O + 11\,H \overset{\checkmark}{=} 1\,As + 4\,Zn + 4\,O + 11\,H$$

   - Charge:

$$8(+1) \overset{\checkmark}{=} 4(+2)$$

The balanced chemical equation (both for charge and for atoms) for this reaction is therefore:

$$H_3AsO_4(aq) + 4\,Zn(s) + 8\,H^+(aq) \longrightarrow AsH_3(g) + 4\,Zn^{2+}(aq) + 4\,H_2O(l)$$

? Exercise 6.2.1: Oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$CuS(s) + H^+(aq) + NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + NO(g) + SO_4^{2-}(aq)$$

Answer

$$3\,CuS(s) + 8\,H^+(aq) + 8\,NO_3^-(aq) \rightarrow 3\,Cu^{2+}(aq) + 8\,NO(g) + 3\,SO_4^{2-}(aq) + 4\,H_2O(l)$$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 6.2.2.

✓ Example 6.2.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$Al(s) + H_2O(l) \rightarrow [Al(OH)_4]^-(aq) + H_2(g)$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example 6.2.1, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.

2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[Al(OH)_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in H_2. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}_{(s)} + \overset{+1}{H}_2O_{(aq)} \rightarrow [\overset{+3}{Al}(OH)_4]^-_{(aq)} + \overset{0}{H}_{2(g)}$$

3. Write separate equations for oxidation and reduction.
   - Reduction:

$$\overset{+1}{H} + e^- \rightarrow \overset{0}{H}\ (in\ H_2)$$

   - Oxidation:

$$\overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$

4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
   - Reduction:

$$3\,H^+ + 3\,e^- \longrightarrow 3\,H^0\ (in\ H_2)$$

   - Oxidation:

$$Al^0 \longrightarrow Al^{3+} + 3\,e^-$$

5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of H_2O contains two protons, in this case, $3\,H^+$ corresponds to $\frac{3}{2}\,H_2O$. Similarly, each molecule of hydrogen gas contains two H atoms, so $3\,H$ corresponds to $\frac{3}{2}\,H_2$.
   - Reduction:

$$\tfrac{3}{2}\,H_2O + 3\,e^- \longrightarrow \tfrac{3}{2}\,H_2$$

   - Oxidation:

$$Al \longrightarrow [Al(OH)_4]^- + 3\,e^-$$

6. Adding the equations and canceling the electrons gives

$$Al + \tfrac{3}{2}\,H_2O + \cancel{3e^-} \longrightarrow [Al(OH)_4]^- + \tfrac{3}{2}\,H_2 + \cancel{3e^-}$$

$$Al + \tfrac{3}{2}\,H_2O \longrightarrow [Al(OH)_4]^- + \tfrac{3}{2}\,H_2$$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2\,Al + 3\,H_2O \rightarrow 2\,[Al(OH)_4]^- + 3\,H_2$$

7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two OH^- ions to the left side:

$$2\,Al + 2\,OH^- + 3\,H_2O \longrightarrow 2\,[Al(OH)_4]^- + 3\,H_2$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three H_2O molecules to the left side:

$$2\,Al + 2\,OH^- + 6\,H_2O \longrightarrow 2\,[Al(OH)_4]^- + 3\,H_2$$

9. Be sure the equation is balanced:
   1. Atoms:

$$2\,Al + 8\,O + 14\,H \overset{\checkmark}{=} 2\,Al + 8\,O + 14\,H$$

   2. Charge:

$$(2)(0) + (2)(-1) + (6)(0) \overset{\checkmark}{=} (2)(-1) + (3)(0)$$

The balanced chemical equation is therefore

$$2\,Al\,(s) + 2\,OH^-\,(aq) + 6\,H_2O\,(l) \rightarrow 2\,[Al(OH)_4]^-\,(aq) + 3\,H_2\,(g)$$

Thus 3 mol of H_2 gas are produced for every 2 mol of Al consumed.

? Exercise 6.2.2: Reducing Manganese in permanganate

The permanganate ion reacts with nitrite ion in basic solution to produce manganese (IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer

$$2\,MnO_4^-\,(aq) + 3\,NO_2^-\,(aq) + H_2O\,(l) \longrightarrow 2\,MnO_2\,(s) + 3\,NO_3^-\,(aq) + 2\,OH^-\,(aq)$$

As suggested in Examples 6.2.1 and 6.2.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^-, NO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4, NH_3, H_2S, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> *Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.*



Balancing a Redox Reaction in Acidic Conditions: Balancing a Redox Reaction in Acidic Conditions (opens in new window) [youtu.be]

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance

oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

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6.3: Voltaic Cells- Generating Electricity from Spontaneous Chemical Reactions

Learning Objectives

- To understand the basics of voltaic cells
- To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$\mathrm{Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)}$$

The half-reactions are as follows:

reduction half-reaction:

$$\mathrm{Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)}$$

oxidation half-reaction:

$$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and $\mathrm{Br_2}$ is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 6.3.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 6.3.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an

electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.

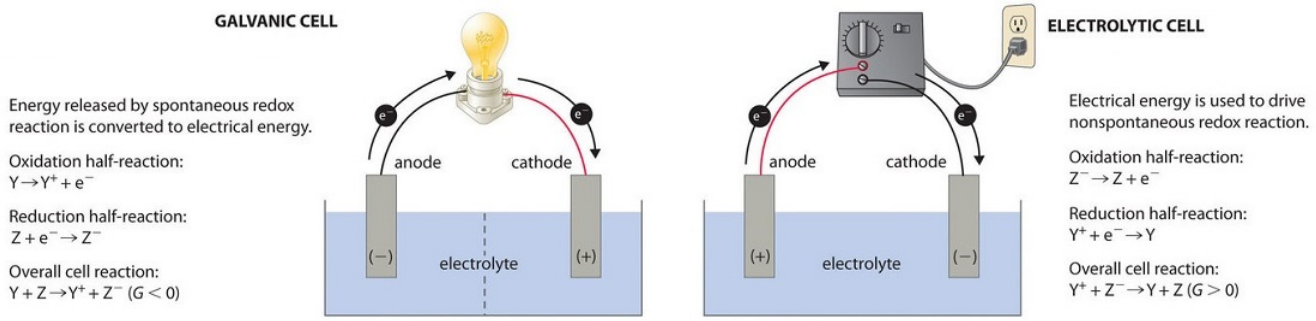


Figure **6.3.1**: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)} \tag{6.3.1}$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.



Figure **6.3.2**: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $\mathrm{Zn^{2+}\,(aq)}$ ions, while $\mathrm{Cu^{2+}\,(aq)}$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure **6.3.3***a*. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of $\mathrm{Cu^{2+}}$ ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of $\mathrm{Zn^{2+}}$ ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte.

The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 6.3.3*b*). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

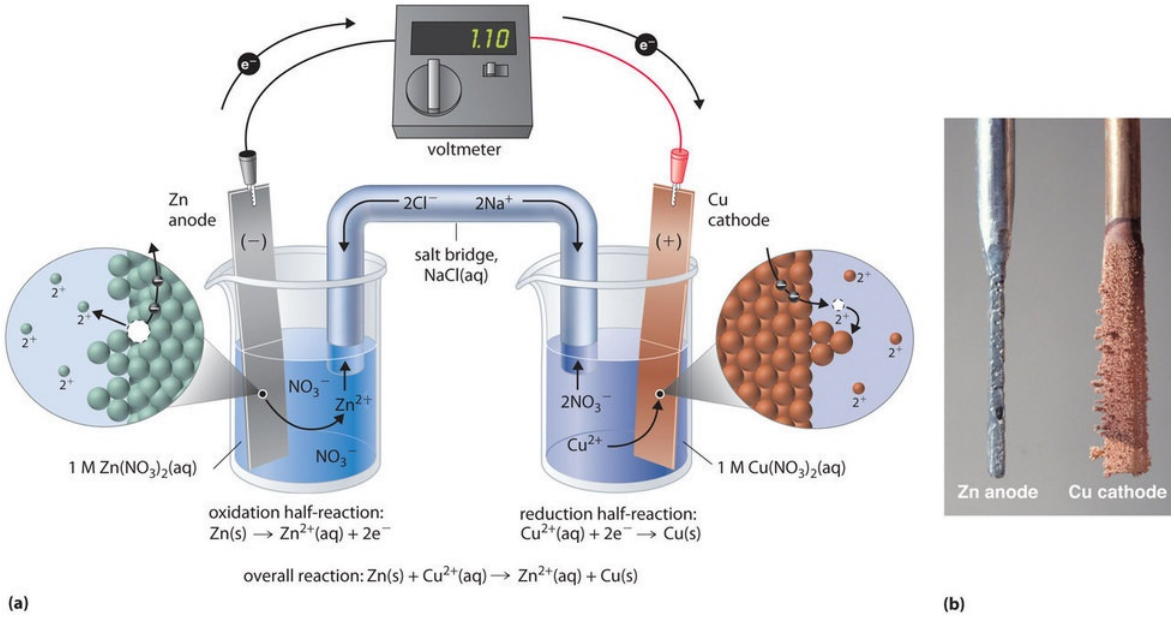


Figure 6.3.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 6.3.3*a*). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example **6.3.1**.

> *A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

Example 6.3.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3\,Sn\,(s) + 2\,NO_3^-\,(aq) + 8\,H^+\,(aq) \rightarrow 3\,Sn^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$NO_3^-\,(aq) + 4\,H^+\,(aq) + 3\,e^- \longrightarrow NO\,(g) + 2\,H_2O\,(l)$$

oxidation:

$$Sn\,(s) \longrightarrow Sn^{2+}\,(aq) + 2\,e^-$$

Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

? Exercise 6.3.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2\,MnO_4^-(aq) + 5\,Sn^{2+}(aq) + 16\,H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,Sn^{4+}(aq) + 8\,H_2O(l)$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is positive and which is negative.

Answer a

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

Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.



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

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the **Zn/Cu** cell shown in Figure **6.3.3***a* is written as follows:

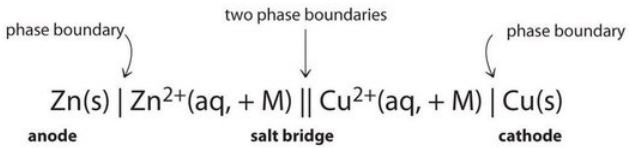


Figure **6.3.4**: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\mathrm{Pt(s)\ |\ H_2(g)\ |\ HCl(aq,\ 1\,M)\ |\ AgCl(s)\ Ag(s)}$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

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

anode reaction:

$$\mathrm{\tfrac{1}{2}\,H_2(g) \longrightarrow H^+(aq) + e^-}$$

overall:

$$\mathrm{AgCl(s) + \tfrac{1}{2}\,H_2(g) \longrightarrow Ag(s) + Cl^- + H^+(aq)}$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

✔ Example 6.3.2

Draw a cell diagram for the galvanic cell described in Example **6.3.1**. The balanced chemical reaction is as follows:

$$\mathrm{3\,Sn(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \rightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)}$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\mathrm{Sn(s)\,|\,Sn^{2+}(aq)}$. We could include $\mathrm{H_2SO_4(aq)}$ with the contents of the anode compartment, but the sulfate ion (as $\mathrm{HSO_4^-}$) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\mathrm{HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\mathrm{Sn(s)\ |\,Sn^{2+}(aq)\,||\,HNO_3(aq)\,|\,NO(g)\,|\,Pt_{(s)}}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

? Exercise 6.3.2

Draw the cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$Mg(s) + 2\,Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2\,Ag(s)$$

Answer

$$Mg(s)\ \left|Mg^{2+}(aq,\ 1\,M)\right|\left|Ag^+(aq,\ 1\ M)\right|\ Ag(s)$$



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

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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6.4: Standard Reduction Potentials

Learning Objectives

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

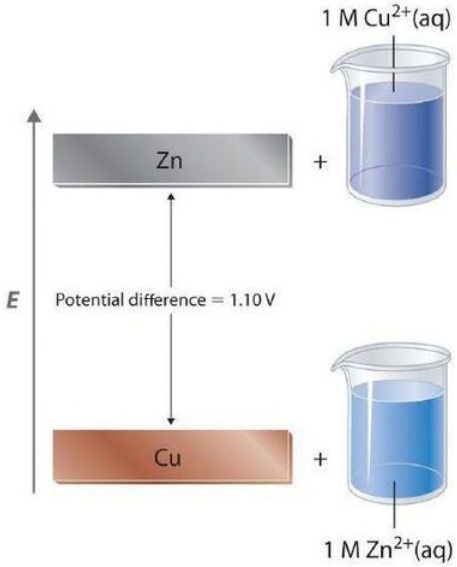


Figure **6.4.1**: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic ***Zn*** and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous ***Zn^{2+}*** ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure **6.4.1** but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E° = 0.59\ V \tag{6.4.1}$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential ($E°_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E°_{cell} = E°_{cathode} - E°_{anode} \tag{6.4.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 6.4.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

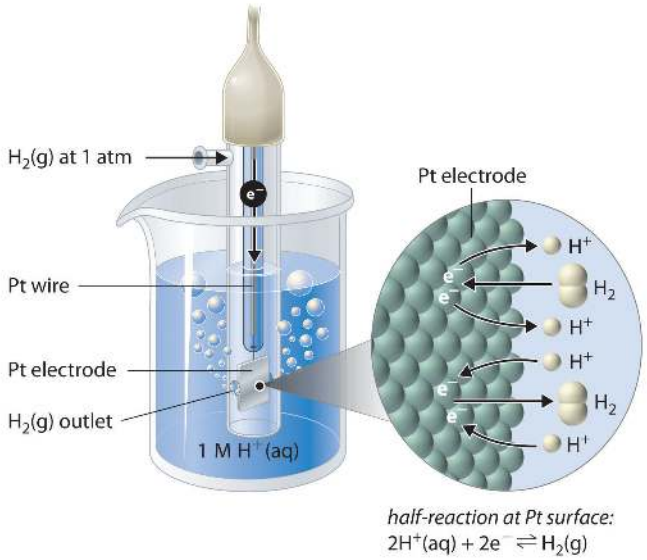


Figure 6.4.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 6.4.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{6.4.3}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

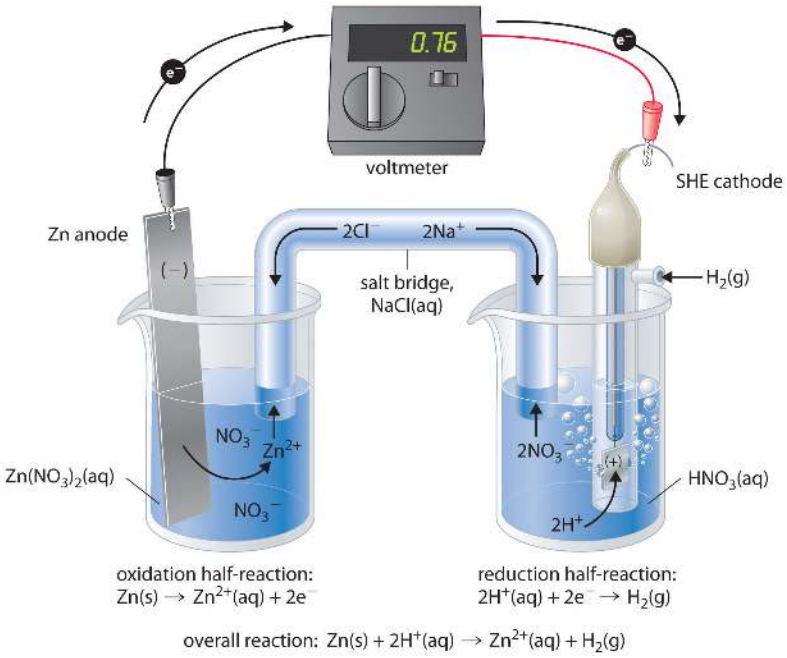


Figure **6.4.3**: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form $Zn^{2+}(aq)$ ions while $H^+(aq)$ ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Figure **6.4.3** shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{6.4.4}$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{6.4.5}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{6.4.6}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{6.4.7}$$

We then use Equation 6.4.2 to calculate the cell potential

$$\begin{aligned} E°_{cell} &= E°_{cathode} - E°_{anode} \\ &= 0.76\ V \end{aligned}$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ is −0.76 V, which means that the

standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn^{2+}, often called the Zn/Zn^{2+} redox couple, or the Zn/Zn^{2+} couple, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain

$$E°_{cell} : 0\,V - (-0.76\,V) = 0.76\,V$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*



The Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE)(opens in new window) [youtu.be]

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure **6.4.3** but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{6.4.8}$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\ V \tag{6.4.9}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\ V \tag{6.4.10}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{6.4.11}$$

We then use Equation **6.4.2** to calculate the cell potential

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.34\ V$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.



Electrode Potentials and ECell: Electrode and Potentials and Ecell(opens in new window) [youtu.be]

Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{6.4.12}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to $H_2$and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{6.4.13}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{6.4.14}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 6.4.13, two H^+ ions gain one electron each in the reduction; in Equation 6.4.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 6.4.13) by 3 and the oxidation half-reaction (Equation 6.4.14) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{6.4.15}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{6.4.16}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{6.4.17}$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{6.4.18}$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{6.4.19}$$

The atoms also balance, so Equation 6.4.18 is a balanced chemical equation for the redox reaction depicted in Equation 6.4.12.

> *The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 6.4.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{6.4.20}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{6.4.21}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{6.4.22}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{6.4.23}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{6.4.24}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{6.4.25}$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al° to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{6.4.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{6.4.27}$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 6.4.26 (the reductive half-reaction) by 3 and Equation 6.4.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{6.4.28}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{6.4.29}$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{6.4.30}$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{6.4.31}$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 6.4.31 is identical to Equation 6.4.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

Example 6.4.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}(aq)$ complex and brown $I_2(aq)$ ions (Figure 6.4.4):

$$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Table P1

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution

From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:

- reduction:

$$\mathrm{Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)}$$

- oxidation:

$$\mathrm{2\,I^-(aq) \longrightarrow I_2(aq) + 2\,e^-}$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$\mathrm{6\,I^-(aq) \longrightarrow 3\,I_2(aq) + 6\,e^-}$$

Adding the two half-reactions and canceling electrons,

$$\mathrm{Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) + 3\,I_2(aq)}$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$
$$+6 \overset{\checkmark}{=} +6$$

and atoms

$$\mathrm{2\,Cr + 7\,O + 14\,H + 6\,I \overset{\checkmark}{=} 2\,Cr + 7\,O + 14\,H + 6\,I}$$

Both the charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from $\mathrm{Cr^{6+}}$ in $\mathrm{Cr_2O_7^{2-}}$ to $\mathrm{Cr^{3+}}$, and $\mathrm{I^-}$ ions are oxidized to $\mathrm{I_2}$. Dividing the reaction into two half-reactions,

- reduction:

$$\mathrm{Cr_2O_{7(aq)}^{2-} \rightarrow Cr_{(aq)}^{3+}}$$

- oxidation:

$$\mathrm{I_{(aq)}^{-} \rightarrow I_{2(aq)}}$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$\mathrm{Cr_2O_{7(aq)}^{2-} \rightarrow 2Cr_{(aq)}^{3+}}$$

- oxidation:

$$\mathrm{2I_{(aq)}^{-} \rightarrow I_{2(aq)}}$$

We now balance the O atoms by adding $\mathrm{H_2O}$—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$\mathrm{Cr_2O_{7(aq)}^{2-} \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}}$$

Next we balance the H atoms by adding $\mathrm{H^+}$ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O_{7(aq)}^{2-} + 14H_{(aq)}^{+} \rightarrow 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6I^-(aq) \rightarrow 3I_2(s) + 6e^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$\mathrm{Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,I^-\,(aq) \longrightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l) + 3\,I_2\,(aq)}$$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

? Exercise 6.4.1

Copper is found as the mineral covellite (**CuS**). The first step in extracting the copper is to dissolve the mineral in nitric acid ($\mathbf{HNO_3}$), which oxidizes sulfide to sulfate and reduces nitric acid to **NO**:

$$\mathrm{CuS\,(s) + HNO_3\,(aq) \rightarrow NO\,(g) + CuSO_4\,(aq)}$$

Balance this equation using the half-reaction method.



Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer

$$\mathrm{3\,CuS\,(s) + 8\,HNO_3\,(aq) \longrightarrow 8\,NO\,(g) + 3\,CuSO_4\,(aq) + 4\,H_2O\,(l)}$$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{6.4.32}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:

$$Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{6.4.33}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{6.4.34}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{6.4.35}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example **6.4.2** and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

Example 6.4.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$\text{cathode: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B. Use Equation 6.4.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 6.4.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$0.27\ V = E°°_{cathhode} - (-0.55\ V)$$

$$E°_{cathode} = -0.28\ V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\ V) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

? Exercise 6.4.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $\mathbf{Hg(CH_3CO_2)_2}$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $\mathbf{MgCl_2}$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $\mathbf{Hg^{2+}(aq) + 2\,e^- \longrightarrow Hg(l)}$
- anode: $\mathbf{Mg(s) \longrightarrow Mg^{2+}(aq) + 2\,e^-}$

If the potential for the oxidation of $\mathbf{Mg}$ to $\mathbf{Mg^{2+}}$ is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

Answer

0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{6.4.36}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 6.4.5. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{6.4.37}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{6.4.38}$$

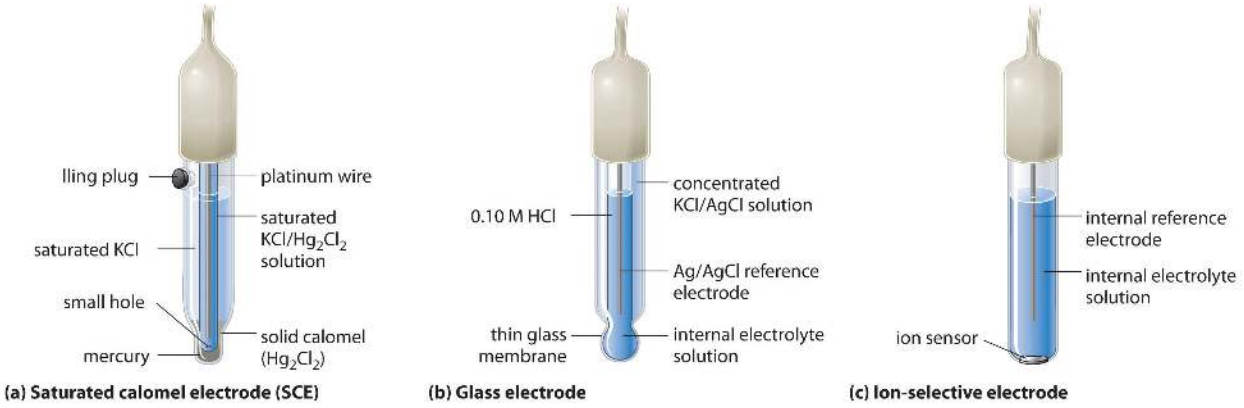


Figure 6.4.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 6.4.5. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that $pH = -\log[H^+]$):

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{6.4.39}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 6.4.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 6.4.1.

Table 6.4.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} − E°_{anode} \nonumber \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

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6.5: Cell Potential, Gibbs Energy, and the Equilibrium Constant

Learning Objectives

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of $\mathrm{Co(s)}$ with $\mathrm{Ni^{2+}(aq)}$ to form $\mathrm{Ni(s)}$ and $\mathrm{Co^{2+}(aq)}$ occurs spontaneously, but if we reduce the concentration of $\mathrm{Ni^{2+}}$ by a factor of 100, so that $[\mathrm{Ni^{2+}}]$ is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential & Gibbs Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in **coulombs (C)**, an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in **amperes (A)**; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ \mathrm{J}}{1\ \mathrm{V}} = 1\ \mathrm{C} = \mathrm{A \cdot s}$$

In chemical reactions, however, we need to relate the coulomb to the charge on a mole of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the **faraday (F)**, named after the English physicist and chemist Michael Faraday (1791–1867):

$$\begin{aligned} F &= (1.60218 \times 10^{-19}\ \mathrm{C}) \left(\frac{6.02214 \times 10^{23}\ J}{1\ \mathrm{mol\ e^-}} \right) \\ &= 9.64833212 \times 10^{4}\ \mathrm{C/mol\ e^-} \\ &\simeq 96,485\ J/(\mathrm{V \cdot mol\ e^-}) \end{aligned}$$

The total charge transferred from the reductant to the oxidant is therefore nF, where n is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E°_{cell}) and the total charge transferred during the reaction (nF):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done by a system (an electrochemical cell with a positive potential) on its surroundings.

The change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG; this relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a negative value of ΔG and a positive value of E°_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell} \tag{6.5.1}$$

A spontaneous redox reaction is characterized by a negative value of ΔG°, which corresponds to a positive value of E°_{cell}.

Example 6.5.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table P2, calculate the free-energy change (ΔG°) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: ΔG^o for the reaction and spontaneity

Strategy:

A. From the relevant half-reactions and the corresponding values of E^o, write the overall reaction and calculate E°_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Then use Equation 6.5.1 to calculate ΔG^o. If ΔG^o is negative, then the reaction is spontaneous.

Solution

A

As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of E^o. From Table P2, we can find the reduction and oxidation half-reactions and corresponding E^o values:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$	$E^\circ_{anode} = 1.09\ V$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of E^o is not affected:

cathode:	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	$E^\circ_{cathode} = 1.36\ V$
anode:	$6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^-$	$E^\circ_{anode} = 1.09\ V$
overall:	$Cr_2O_7^{2-}(aq) + 6Br^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Br_2(aq) + 7H_2O(l)$	$E^\circ_{cell} = 0.27\ V$

B

We can now calculate ΔG° using Equation 6.5.1. Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned}\Delta G^\circ &= -(n)(F)(E^\circ_{cell}) \\ &= -(6\text{ mole})[96,485\text{ J/(V}\cdot\text{mol)}(0.27\text{ V})] \\ &= -15.6 \times 10^4\text{ J} \\ &= -156\text{ kJ/mol } Cr_2O_7^{2-}\end{aligned}$$

Thus ΔG^o is −168 kJ/mol for the reaction as written, and the reaction is spontaneous.

Exercise 6.5.1

Use the data in Table P2 to calculate ΔG^o for the reduction of ferric ion by iodide:

$$2\,Fe^{3+}(aq) + 2\,I^-(aq) \longrightarrow 2\,Fe^{2+}(aq) + I_2(s)$$

Is the reaction spontaneous?

Answer

−44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table P2 list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of $\mathrm{Fe^{3+}(aq)}$ to $\mathrm{Fe(s)}$ is not listed in the table, but two related reductions are given:

$$\mathrm{Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)} \quad E^\circ = +0.77V$$

$$\mathrm{Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)} \quad E^\circ = -0.45V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction because E^o is not a state function. However, because ΔG^o is a state function, the sum of the ΔG^o values for the individual reactions gives us ΔG^o for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. To obtain the value of E^o for the overall half-reaction, we first must add the values of $\Delta G^o (= -nFE^o)$ for each individual half-reaction to obtain ΔG^o for the overall half-reaction:

Extra close brace or missing open brace

Solving the last expression for ΔG° for the overall half-reaction,

$$\Delta G^\circ = F[(-0.77V) + (-2)(-0.45V)] = F(0.13V)$$

Three electrons ($n = 3$) are transferred in the overall reaction, so substituting into Equation 6.5.1 and solving for E^o gives the following:

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ F(0.13\text{ V}) &= -(3)(F)(E^\circ_{\text{cell}}) \\ E^\circ &= -\frac{0.13\text{ V}}{3} = -0.043\text{ V} \end{aligned}$$

This value of E^o is very different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

> *Values of E^o for half-reactions cannot be added to give E^o for the sum of the half-reactions; only values of $\Delta G^o = -nFE^\circ_{cell}$ for half-reactions can be added.*

The Relationship between Cell Potential & the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K, to obtain a relationship between E°_{cell} and K. Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

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

Given the relationship between the standard free-energy change and the standard cell potential (Equation 6.5.1), we can write

$$-nFE^\circ_{cell} = -RT \ln K$$

Rearranging this equation,

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{6.5.2}$$

For $T = 298\,K$, Equation 6.5.2 can be simplified as follows:

$$
\begin{aligned}
E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \\
&= \left[\frac{[8.314\ \text{J/(mol}\cdot\text{K)}(298\ \text{K})]}{n[96,485\ \text{J/(V}\cdot\text{mol)}]}\right] 2.303 \log K \\
&= \left(\frac{0.0592\ \text{V}}{n}\right) \log K
\end{aligned} \tag{6.5.3}
$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Example 6.5.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A. Write the relevant half-reactions and potentials. From these, obtain the overall reaction and E^o_{cell}.

B. Determine the number of electrons transferred in the overall reaction. Use Equation 6.5.3 to solve for $\log K$ and then K.

Solution

A The relevant half-reactions and potentials from Table P2 are as follows:

cathode:	$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	$E^\circ_{\text{cathode}} = 1.69\ \text{V}$
anode:	$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	$E^\circ_{\text{anode}} = -0.36\ \text{V}$
overall:	$Pb(s) + PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$	$E^\circ_{\text{cell}} = 2.05\ \text{V}$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 6.5.3 for log K and inserting the values of n and E^o,

$$
\log K = \frac{nE^\circ}{0.0591\ \text{V}} = \frac{2(2.05\ \text{V})}{0.0591\ \text{V}} = 69.37
$$

$$
K = 2.3 \times 10^{69}
$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

Exercise 6.5.2

Use the data in Table P2 to calculate the equilibrium constant for the reaction of $Sn^{2+}(aq)$ with oxygen to produce $Sn^{4+}(aq)$ and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

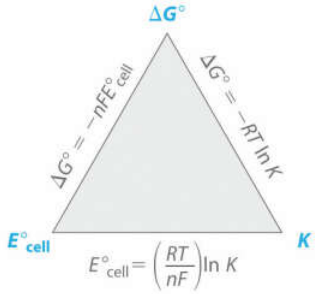
$$
2\,Sn^{2+}(aq) + O_2(g) + 4\,H^+(aq) \rightleftharpoons 2\,Sn^{4+}(aq) + 2\,H_2O(l)
$$

Answer

5.7×10^{72}

Figure 6.5.1 summarizes the relationships that we have developed based on properties of the system—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G^\circ < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation

that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q.



$\Delta G°$	$E°_{cell}$	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure **6.5.1**: The Relationships among Criteria for Thermodynamic Spontaneity. The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, ΔG°, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of ΔG° and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions. (CC BY-NC-SA; Anonymous by request)

If ΔG is less than zero, E^o is greater than zero and K is greater than 1 then the direction of the reaction is spontaneous in forward direction. If ΔG is greater than zero, E^o is less than zero and K is less than one then the direction of reaction is spontaneous in reverse direction. If ΔG is zero, E is zero and K is one that there is no net reaction and the system is at equilibrium .

Summary

A coulomb (C) relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in amperes (A), where 1 A is defined as the flow of 1 C/s past a given point. The faraday (F) is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to both the potential and the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of E°.

6.5: Cell Potential, Gibbs Energy, and the Equilibrium Constant is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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6.6: Cell Potential and Concentration (Nernst Equation)

Learning Objectives

- Relate cell potentials to Gibbs energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants (including solubility constants).

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall that the actual free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{6.6.1}$$

We also know that $\Delta G = -nFE_{cell}$ (under non-standard conditions) and $\Delta G^o = -nFE^o_{cell}$ (under standard conditions). Substituting these expressions into Equation 6.6.1, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT \ln Q \tag{6.6.2}$$

Dividing both sides of this equation by $-nF$,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln Q \tag{6.6.3}$$

Equation 6.6.3 is called the **Nernst equation**, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), then Equation 6.6.3 reduces to Equation 6.6.4 and 6.6.5 because $Q = K$, and there is no net transfer of electrons (i.e., E_{cell} = 0).

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF}\right) \ln K = 0 \tag{6.6.4}$$

since

$$E^\circ_{\text{cell}} = \left(\frac{RT}{nF}\right) \ln K \tag{6.6.5}$$

Substituting the values of the constants into Equation 6.6.3 with $T = 298\ K$ and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \tag{6.6.6}$$

The Power of the Nernst Equation

The Nernst Equation (6.6.3) can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 6.6.6 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 6.6.6 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 6.6.1

The following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which means that $\Delta G° < 0$):

$$2\,Ce^{4+}(aq) + 2\,Cl^-(aq) \longrightarrow 2\,Ce^{3+}(aq) + Cl_2(g) \qquad E°_{cell} = 0.25\,V$$

Calculate E_{cell} for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: $[Ce^{4+}] = 0.013$ M, $[Ce^{3+}] = 0.60$ M, $[Cl^-] = 0.0030$ M, $P_{Cl_2} = 1.0$ atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 6.6.6 instead of Equation 6.6.3. The overall reaction involves the net transfer of two electrons:

$$2Ce^{4+}_{(aq)} + 2e^- \rightarrow 2Ce^{3+}_{(aq)}$$

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 6.6.6,

$$\begin{aligned} E_{cell} &= E°_{cell} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0.25\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right)\log\left(\frac{[Ce^{3+}]^2 P_{Cl_2}}{[Ce^{4+}]^2[Cl^-]^2}\right) \\ &= 0.25\ \text{V} - [(0.0296\ \text{V})(8.37)] = 0.00\ \text{V} \end{aligned}$$

Thus the reaction will not occur spontaneously under these conditions (because E = 0 V and $\Delta G = 0$). The composition specified is that of an equilibrium mixture

Exercise 6.6.1

Molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4\,MnO_2(s) + 3\,O_2(g) + 4\,OH^-(aq) \longrightarrow 4\,MnO_4^-(aq) + 2\,H_2O(l) \quad E°_{cell} = -0.20\,V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, P_{O_2} = 0.20 atm, $[MNO_4^-] = 1.0 \times 10^{-4}$ M, and T = 25°C.

Answer

$E_{cell} = -0.22$ V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \quad E°cell = 1.10V \tag{6.6.7}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0×10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 6.6.6:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \tag{6.6.8}$$

$$= 1.10\ V - \left(\frac{0.0591\ V}{2}\right) \log \left(\frac{1.0 \times 10^{-6}}{1.0}\right) = 1.28\ V \tag{6.6.9}$$

Thus the initial voltage is greater than E° because $Q < 1$. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so $Q = 1$ and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0×10^{-6} M Cu^{2+}), $Q = 1.0 \times 10^6$, and the cell potential will be reduced to 0.92 V.

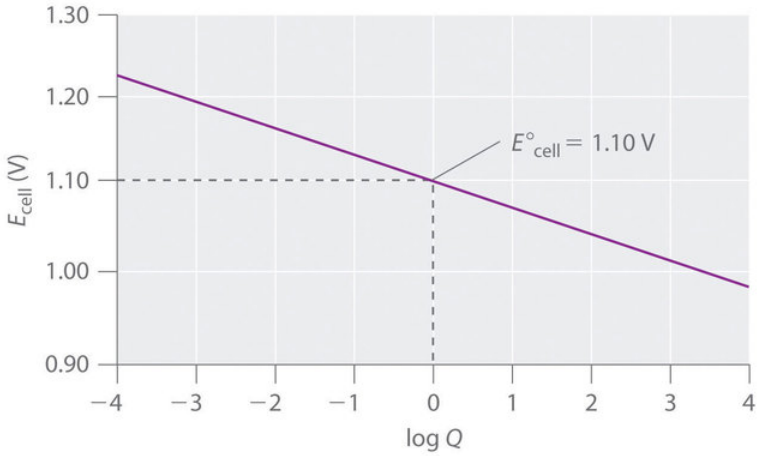


Figure **6.6.1**: The Variation of E_{cell} with Log Q for a Zn/Cu Cell. Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell} = 1.10$ V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until Q = K and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

The variation of E_{cell} with $\log Q$ over this range is linear with a slope of −0.0591/n, as illustrated in Figure **6.6.1**. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when $E_{cell} = 0$ is calculated as follows:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ V}{n}\right) \log Q = 0 \tag{6.6.10}$$

$$E^\circ = \left(\frac{0.0591\ V}{n}\right) \log Q \tag{6.6.11}$$

$$\log Q = \frac{E°n}{0.0591\ V} = \frac{(1.10\ V)(2)}{0.0591\ V} = 37.23 \tag{6.6.12}$$

$$Q = 10^{37.23} = 1.7 \times 10^{37} \tag{6.6.13}$$

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.



The Nernst Equation: The Nernst Equation (opens in new window) [youtu.be]

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$\mathrm{Ag(s)\,|\,Ag^+}(aq, 0.010\ M)\ ||\ \mathrm{Ag^+}(aq, 1.0\ M)\,|\,\mathrm{Ag\,(s)} \tag{6.6.14}$$

cathode:

$$\mathrm{Ag^+}(aq, 1.0\ M) + \mathrm{e^-} \rightarrow \mathrm{Ag\,(s)} \tag{6.6.15}$$

anode:

$$\mathrm{Ag\,(s)} \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) + \mathrm{e^-} \tag{6.6.16}$$

Overall

$$\mathrm{Ag^+}(aq, 1.0\ M) \rightarrow \mathrm{Ag^+}(aq, 0.010\ M) \tag{6.6.17}$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $Ag(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log Q \\ &= 0 - \left(\frac{0.0591\ \text{V}}{1}\right)\log\left(\frac{0.010}{1.0}\right) \\ &= 0.12\ \text{V} \end{aligned}$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{cell} = 0$).

✔ Example 6.6.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A. Write the overall reaction that occurs in the cell.

B. Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$$\mathrm{Mn^{2+}}(aq, 2.0\,M) \rightarrow \mathrm{Mn^{2+}}(aq, 5.2 \times 10^{-2}\,M)$$

B For the reduction of Mn^{2+}(aq) to Mn(s), n = 2. We substitute this value and the given Mn^{2+} concentrations into Equation 6.6.6:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log Q \\ &= 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log\left(\frac{5.2 \times 10^{-2}}{2.0}\right) \\ &= 0.047\ \text{V} \end{aligned}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 6.6.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with P_{O_2} = 0.20 atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:

$$\mathrm{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \rightarrow 2\,H_2O\,(l)}$$

What will be the potential when the circuit is closed?

Answer

0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned previously, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

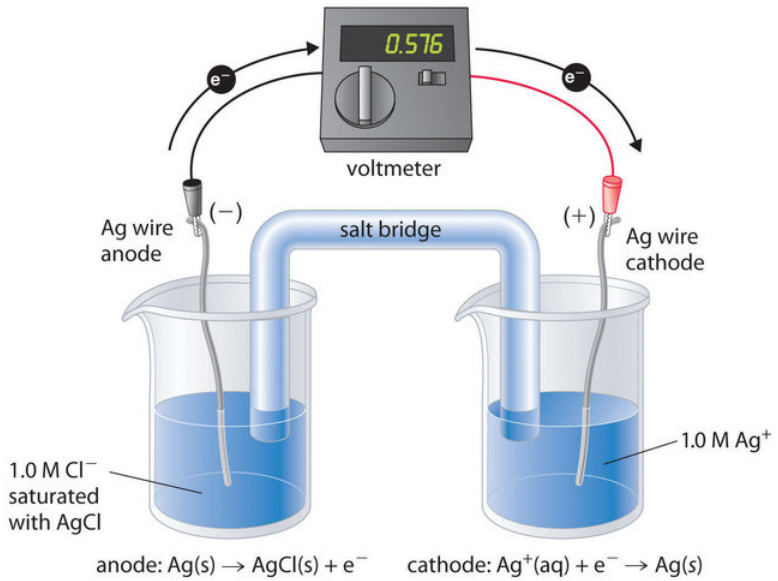


Figure **6.6.1**: A Galvanic ("Concentration") Cell for Measuring the Solubility Product of AgCl. One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}. (CC BY-NC-SA; Anonymous by request)

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure **6.6.1**, which is designed to measure the solubility product of silver chloride:

$$K_{sp} = [Ag^+][Cl^-].$$

In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting:

$$\begin{aligned}[Ag^+] &= \frac{K_{sp}}{[Cl^-]} \\ &= \frac{K_{sp}}{1.0} = K_{sp}.\end{aligned}$$

The overall cell reaction is as follows:

$$Ag^+(aq, \text{concentrated}) \rightarrow Ag^+(aq, \text{dilute})$$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$\begin{aligned}E_{cell} &= 0\ V - \left(\frac{0.0591\ V}{1}\right) \log\left(\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}\right) \\ &= -0.0591\ V\ \log\left(\frac{K_{sp}}{1.0}\right) \\ &= -0.0591\ V\ \log K_{sp} \qquad (6.6.18)\end{aligned}$$

By closing the circuit, we can measure the potential caused by the difference in [Ag+] in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 6.6.18 for K_{sp},

$$\begin{aligned}\log K_{sp} &= \frac{-E_{cell}}{0.0591\ V} = \frac{-0.580\ V}{0.0591\ V} = -9.81 \\ K_{sp} &= 1.5 \times 10^{-10}\end{aligned}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 6.6.3: Solubility of lead(II) sulfate

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure **6.6.1**, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A. From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B. Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation ??? and solve for K_{sp}.

Solution

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of $\mathbf{Pb^{2+}}$ and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}][SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ \text{M}} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

$$Pb^{2+}(aq, \text{concentrated}) \rightarrow Pb^{2+}(aq, \text{dilute})$$

so

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591}{n}\right) \log Q$$

$$0.230\ \text{V} = 0\ \text{V} - \left(\frac{0.0591\ \text{V}}{2}\right) \log \left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ \text{V} \log \left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = \log K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise 6.6.3

A concentration cell similar to the one described in Example **6.6.3** contains a 1.0 M solution of lanthanum nitrate [$La(NO_3)_3$] in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer

5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example **6.6.3**, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated below.

Example 6.6.4: Measuring pH

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment. The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$$\mathrm{Zn\,(s)\,|Zn^{2+}}(aq, 1.0\,M)\,\|\,\mathrm{H^+}(aq, ?\,M)\,|\,\mathrm{H_2}(g, 1.0\,atm)|Pt(s)$$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A. Write the overall cell reaction.
B. Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table P2):

$$Zn(s) + 2H^{2+}(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad E°=0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 6.6.6), we can calculate $[H^+]$ under nonstandard conditions:

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591\ \mathrm{V}}{n}\right)\log\left(\frac{[\mathrm{Zn^{2+}}]P_{\mathrm{H_2}}}{[\mathrm{H^+}]^2}\right)$$

$$0.26\ \mathrm{V} = 0.76\ \mathrm{V} - \left(\frac{0.0591\ \mathrm{V}}{2}\right)\log\left(\frac{(1.0)(1.0)}{[\mathrm{H^+}]^2}\right)$$

$$16.9 = \log\left(\frac{1}{[\mathrm{H^+}]^2}\right) = \log[\mathrm{H^+}]^{-2} = (-2)\log[\mathrm{H^+}]$$

$$8.46 = -\log[\mathrm{H^+}]$$

$$8.5 = \mathrm{pH}$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise 6.6.4

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows:

$$Pb_{(s)}\ |\ Pb^{2+}(aq, ?M)\ \|\ H^+(aq), 1.0M\ |\ O_2(g, 1.0atm)\ |\ Pt_{(s)}$$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table P2 to determine the concentration of Pb^{2+} in the groundwater.

Answer

$1.2 \times 10^{-9}\ M$

Summary

The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution. The Nernst equation allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. Concentration cells consist of anode and cathode compartments that are identical

except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

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6.7: Batteries- Using Chemistry to Generate Electricity

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure **6.7.1**). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

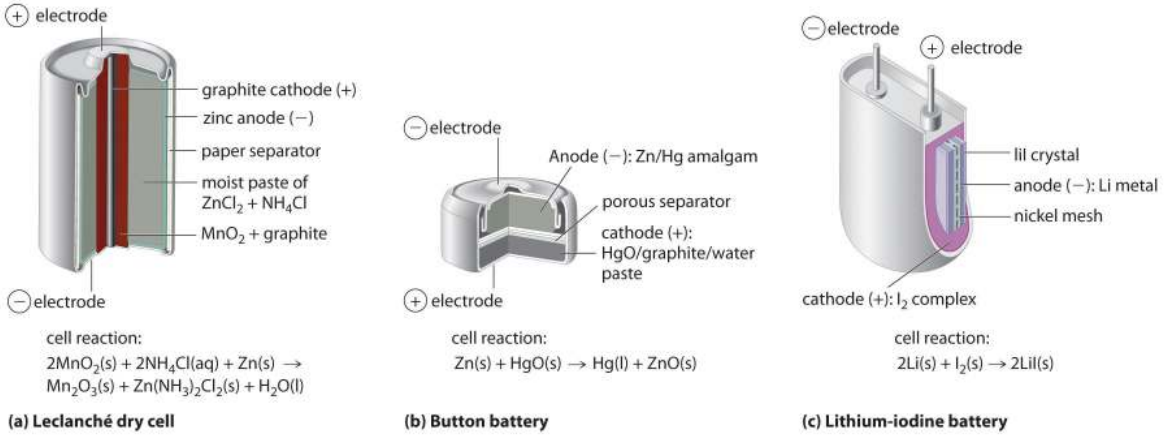


Figure **6.7.1**: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure **6.7.1**). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,MnO_2\,(s) + 2\,NH_4^+\,(aq) + 2\,e^- \longrightarrow Mn_2O_3\,(s) + 2\,NH_3\,(aq) + H_2O\,(l)$$

- anode (oxidation):

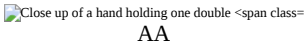
$$Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2\,e^-$$

The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \tag{6.7.1}$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.



AA

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Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

- overall reaction:

$$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 6.7.1*b*).



Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$

- Anode (mercury battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$

- overall reaction (mercury battery):

$$Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)$$

  with $E_{cell} = 1.35\,V$.
- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq)$$

- anode (silver battery):

$$Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$

- Overall reaction (silver battery):

$$Zn(s) + 2Ag_2O(s) \longrightarrow 2Ag(s) + ZnO(s)$$

with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as **Hg** and **Ag**.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-_{(LiI)} \tag{6.7.2}$$

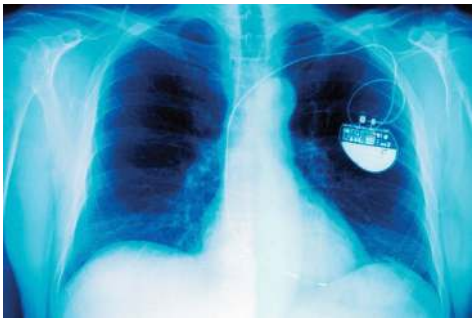
- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{6.7.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{6.7.4}$$

with $E_{cell} = 3.5\,V$



Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure **6.7.1**, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure **6.7.2**, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

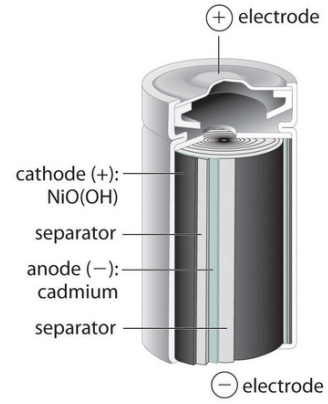


Figure 6.7.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a ***NiCad*** battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{6.7.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{6.7.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{6.7.7}$$

$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

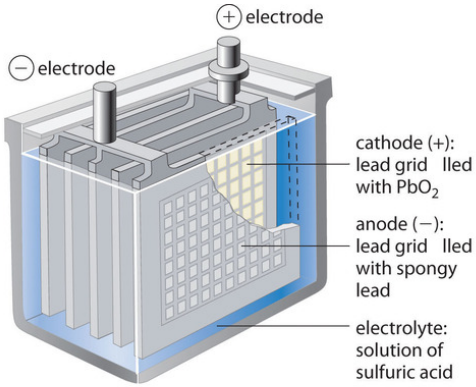
\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells.



cell reaction:

$Pb(s) + PbO_2(s) + 2HSO_4^-(aq) + 2H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Figure **6.7.3**: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure **6.7.3**, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (***PbO_2***). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M ***H_2SO_4***). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

\[PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17} \]

with $E^\circ_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{6.7.8}$$

with $E^\circ_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{6.7.9}$$

and $E^\circ_{cell} = 2.041\ V$

As the cell is discharged, a powder of ***$PbSO_4$*** forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.



A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{6.7.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

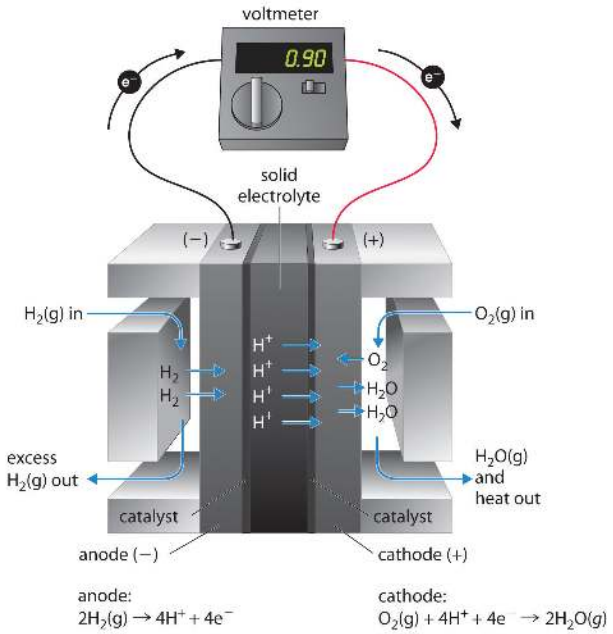


Figure **6.7.4**: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure **6.7.4**. The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{6.7.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{6.7.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{6.7.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

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6.8: Electrolysis- Driving Non-spontaneous Chemical Reactions with Electricity

Learning Objectives

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure **6.8.1***a*).

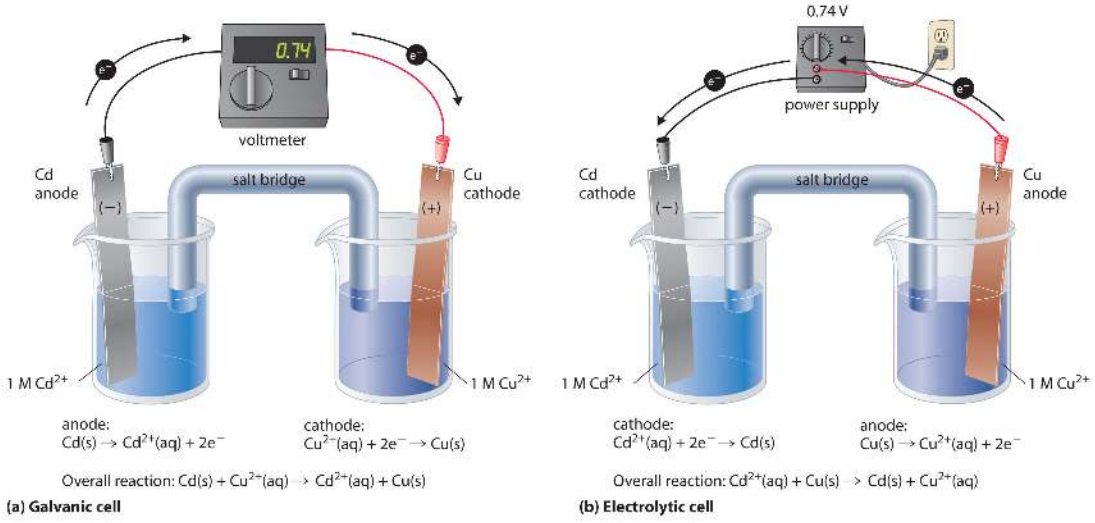


Figure **6.8.1**: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$\mathrm{Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cd^{2+}\,(aq) + Cu\,(s)}$$

with $E°_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G° < 0$):

$$\begin{aligned}\Delta G° &= -nFE°_{\text{cell}} \\ &= -(2\ \text{mol e}^-)[96,485\ \text{J/(V}\cdot\text{mol)}](0.74\ \text{V}) \\ &= -140\ \text{kJ (per mole Cd)}\end{aligned}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure **6.8.1***b*). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$\mathrm{Cd^{2+}(aq) + 2\,e^- \rightarrow Cd(s)} \tag{6.8.1}$$

with $E^\circ_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-} \tag{6.8.2}$$

with $E^\circ_{anode} = 0.34\,V$

- Overall Reaction:

$$\mathrm{Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)} \tag{6.8.3}$$

with $E^\circ_{cell} = -0.74\,V$

Because $E^\circ_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table **6.8.1**.

Table **6.8.1**: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten **NaCl**, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$\mathrm{2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g)} \tag{6.8.4}$$

This is the reverse of the formation of **NaCl** from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of **NaCl** (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten **NaCl** in a Downs cell (Figure **6.8.2**). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the **NaCl** to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

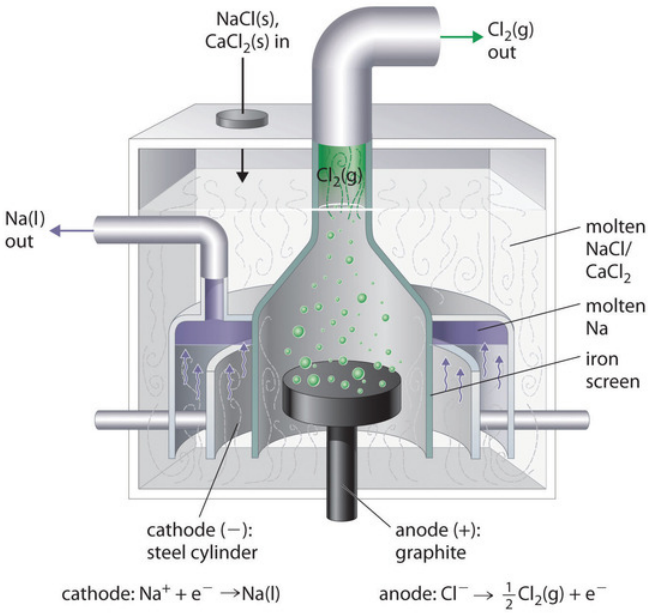


Figure 6.8.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,Al_2O_3\,(l) + 3\,C\,(s) \longrightarrow 4\,Al\,(l) + 3\,CO_2\,(g) \tag{6.8.5}$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

✔ Example 6.8.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.

B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 6.8.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure **6.8.3**).

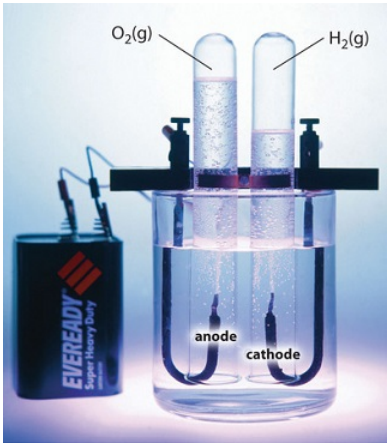


Figure **6.8.3**: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \tag{6.8.6}$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \tag{6.8.7}$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \tag{6.8.8}$$

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2}$ = 1 atm, we can use the standard

potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right)\log(P_{\text{O}_2}P_{\text{H}_2}^2) \tag{6.8.9}$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right)\log(1) = -1.23\ \text{V} \tag{6.8.10}$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 6.8.4.

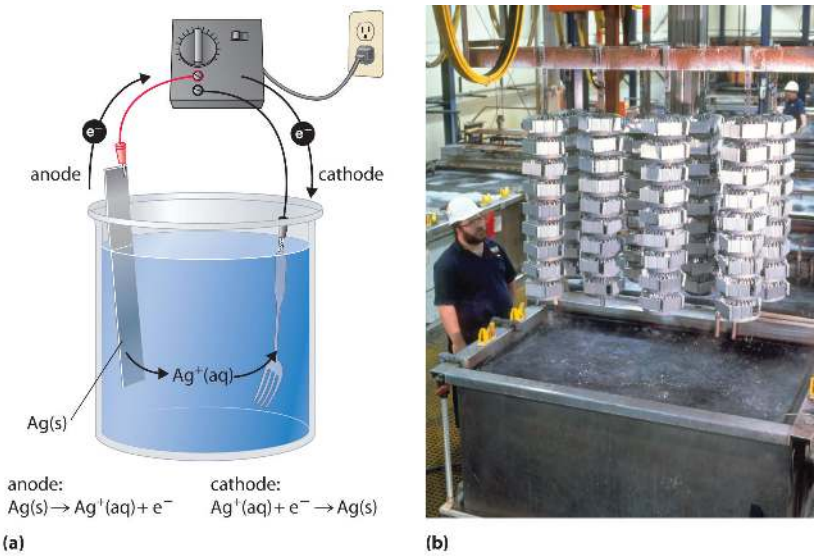


Figure **6.8.3**: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the $\mathbf{Ag^+}$ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad E°_{cathode} = 0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq) + e^-} \qquad E°_{anode} = 0.80V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell} = 0\,V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)}$$

1 mol of electrons reduces 1 mol of $\mathbf{Ag^+}$ to $\mathbf{Ag}$ metal. In contrast, in the reaction

$$\mathrm{Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)}$$

1 mol of electrons reduces only 0.5 mol of $\mathbf{Cu^{2+}}$ to $\mathbf{Cu}$ metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{6.8.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$\begin{aligned} q &= (0.60\ \text{A})(6.0\ \text{min})(60\ \text{s/min}) \\ &= 220\ \text{A} \cdot \text{s} \\ &= 220\ \text{C} \end{aligned}$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$\begin{aligned} \text{moles e}^- &= \frac{220\ \text{C}}{96{,}485\ \text{C/mol}} \\ &= 2.3 \times 10^{-3}\ \text{mol e}^- \end{aligned}$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

Example 6.8.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A. Calculate the number of moles of metal corresponding to the given mass transferred.

B. Write the reaction and determine the number of moles of electrons required for the electroplating process.

C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00\ \text{g}}{107.868\ \text{g/mol}} = 1.85 \times 10^{-2}\ \text{mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}485\ \text{C/mol e}^-) = 1.78 \times 10^3\ \text{C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\begin{aligned} \text{amperes} &= \frac{1.78 \times 10^3\ \text{C}}{(12.0\ \text{h})(60\ \text{min/h})(60\ \text{s/min})} \\ &= 4.12 \times 10^{-2}\ \text{C/s} = 4.12 \times 10^{-2}\ \text{A} \end{aligned}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

? Exercise 6.8.2

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

5.8 h



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

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

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6.9: Corrosion- Undesirable Redox Reactions

Learning Objectives

- To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

> *Corrosion is a REDOX process.*

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($\mathbf{Fe_2O_3 \cdot \mathit{x}\, H_2O}$), commonly known as rust, that does not provide a tight protective film (Figure **6.9.1**). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.

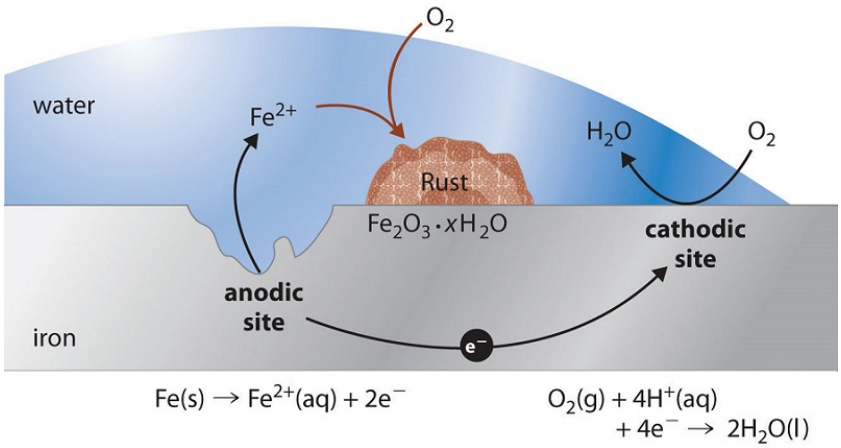


Figure **6.9.1**: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust (Fe_2O_3•xH_2O) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$\mathbf{O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(l)}$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-}$$

with $E^o_{SRP} = -0.45\ V$.

- overall:

$$\mathrm{2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)} \tag{6.9.1}$$

with $E^o_{cell} = 1.68\ V$.

The $\mathrm{Fe^{2+}}$ ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing $\mathrm{Fe^{3+}}$, as represented in the following equation:

$$\mathrm{4Fe^{2+}(aq) + O_2(g) + (2 + 4x)H_2O \ \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+(aq)} \tag{6.9.2}$$

The sign and magnitude of E^o_{cell} for the corrosion process (Equation 6.9.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 6.9.2).

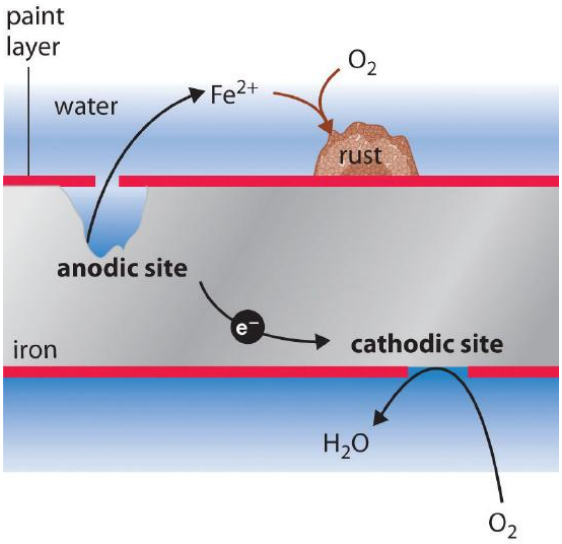


Figure 6.9.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).

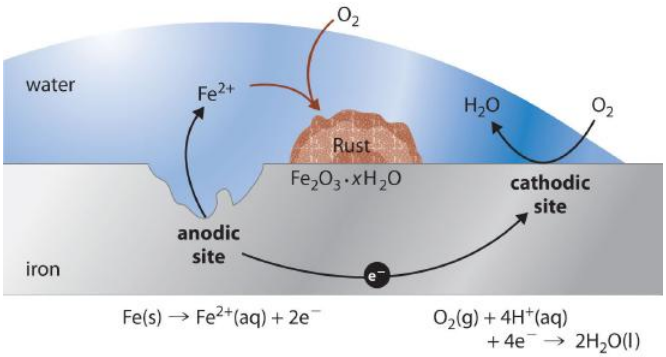


Figure 6.9.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for $\mathbf{Sn^{2+}}$ ($E° = -0.14$ V) and Fe^{2+} ($E° = -0.45$ V) in Table P2 show that **Fe** is more easily oxidized than **Sn**. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 6.9.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as **Zn** ($E° = -0.76$ V for $\mathbf{Zn^{2+} + 2\,e^- \longrightarrow Zn}$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \tag{6.9.3}$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \tag{6.9.4}$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \tag{6.9.5}$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.



Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 6.9.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

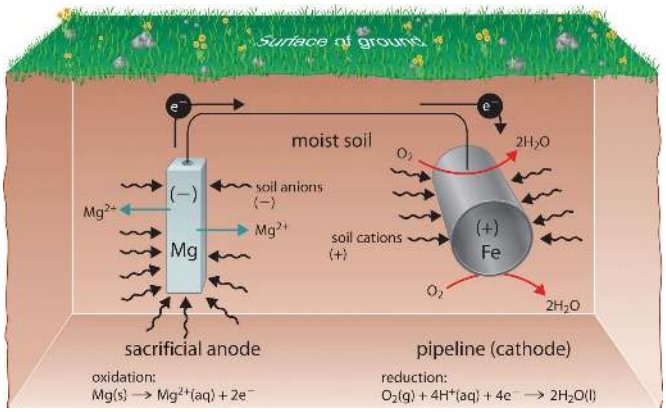


Figure **6.9.4**: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 6.9.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°°_{cell}$?
b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°°_{cell}$, and preventive measures

Strategy:

A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°°_{cell}$.
B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution

a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E°°_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

cathode:	$O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$E°_{cathode} = 1.23\ V$
anode:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$E°_{anode} = -0.45\ V$
overall:	$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$E°_{overall} = 1.68\ V$

Over time, the iron screws will dissolve, and the boat will fall apart.

b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 6.9.5).



Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 6.9.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the **Cu/Fe** pipe joints will lead to rapid corrosion.

Answer b

Any existing **Pb/Fe** joints should be examined carefully for corrosion of the iron pipes due to the **Pb–Fe** junction; the less active **Pb** will have served as the cathode for the reduction of O_2, promoting oxidation of the more active **Fe** nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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6.E: Electrochemistry (Practice problems with Answers)

Questions moved to ADAPT.

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CHAPTER OVERVIEW

7: Nuclear Chemistry

A general chemistry Libretexts Textmap organized around the textbook
General Chemistry -Atoms First
By OpenStax

I *II* *III* *IV* *V* *VI* *VII* *VIII* *IX* *X* *XI* *XII* *XIII* *XIV* *XV* *XVI* *XVII* *XVIII* *XIX* *XX* *XXI* ● **Homework**

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the **electrons** around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions. This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

7.1: Nuclear Structure, Stability, and Binding Energy
7.2: Nuclear Equations
7.3: Radioactive Decay, Half life, and C-14 Dating
7.4: Transmutation and Nuclear Energy
7.5: Uses of Radioisotopes
7.6: Biological Effects of Radiation
7.E: Nuclear Chemistry (Practice Problems with Answers)

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7.1: Nuclear Structure, Stability, and Binding Energy

Learning Objectives

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $^{1}_{1}\mathrm{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term nuclide and identify it by the notation:

$$^{A}_{Z}\mathrm{X} \tag{7.1.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14."

Protons and neutrons, collectively called nucleons, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm^3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger). Example 7.1.1 demonstrates just how great nuclear densities can be in the natural world.

Example 7.1.1: Neutron Stars

Density of a Neutron Star Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass = $M_\odot$ = mass of the sun = 1.99×10^{30} kg) and a diameter of 26 km.

a. What is the density ρ of this neutron star?
b. How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution

We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

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

with

$$V = \frac{4}{3}\pi r^3$$

(a) The radius of the neutron star is $\frac{1}{2} \times 26\ \mathrm{km} = \frac{1}{2} \times 2.6 \times 10^4\ \mathrm{m} = 1.3 \times 10^4\ \mathrm{m}$ so the density of the neutron star is:

$$\begin{aligned}\rho &= \frac{m}{V}\\ &= \frac{m}{\frac{4}{3}\pi r^3}\\ &= \frac{2.4(1.99\times10^{30}\ kg)}{\frac{4}{3}\pi(1.3\times10^{4}m)^3}\\ &= 5.2\times10^{17}\ kg/m^3\end{aligned}$$

(b) The radius of the U-235 nucleus is $\frac{1}{2}\times 15\times10^{-15}\ \text{m} = 7.5\times10^{-15}\ \text{m}$, so the density of the U-235 nucleus is:

$$\begin{aligned}\rho &= \frac{m}{V}\\ &= \frac{m}{\frac{4}{3}\pi r^3}\\ &= \frac{235\ amu\left(\frac{1.66\times10^{-27}\ kg}{1\ amu}\right)}{\frac{4}{3}\pi(7.5\times10^{-15}m)^3}\\ &= 2.2\times10^{17}\ kg/m^3\end{aligned}$$

These values are fairly similar (same order of magnitude), but the nucleus is more than twice as dense as the neutron star.

? Exercise 7.1.1

Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of 1.75 fm ($1\ \text{fm} = 1\times10^{-15}\ \text{m}$).

Answer

The density of the neutron star is $3.4\times10^{18}\ \text{kg/m}^3$. The density of a hydrogen nucleus is $6.0\times10^{17}\ \text{kg/m}^3$. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the strong nuclear force. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underset{\text{protons}}{(2\times1.0073\ \text{amu})} + \underset{\text{neutrons}}{(2\times1.0087\ \text{amu})} + \underset{\text{electrons}}{(2\times0.00055\ \text{amu})} = 4.0331\ \text{amu} \qquad (7.1.2)$$

However, mass spectrometric measurements reveal that the mass of an ^4_2He atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the mass defect indicates a “loss” in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The nuclear binding energy is the energy produced when the atoms’ nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the mass-energy equivalence equation as stated by Albert Einstein:

$$E = mc^2 \tag{7.1.3}$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its **mass defect**, as demonstrated in Example 7.1.2. A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making $\mathbf{1\ eV = 1.602 \times 10^{-19}\ J}$.

Example 7.1.2: Calculation of Nuclear Binding Energy

Determine the binding energy for the nuclide $\mathbf{^4_2He}$ in:

a. joules per mole of nuclei
b. joules per nucleus
c. MeV per nucleus

Solution

The mass defect for a $\mathbf{^4_2He}$ nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

(a) First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of $\mathbf{3.05 \times 10^{-5}\ kg/mol}$. Substituting this quantity into the mass-energy equivalence equation yields:

\[\begin{align*} E &=mc^2 \[4pt] &= \dfrac{3.05 \times 10^{-5}\;kg}{mol} \times \left(\dfrac{2.998 \times 10^8\;m}{s}\right)^2 \[4pt] &= 2.74×10^{12}\:kg\:m^2s^{-2}mol^{-1} \[4pt] &=2.74 \times 10^{12}\;J/mol=2.74\: TJ /mol \end{align*} \nonumber \]

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

(b) The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12}\ J\ mol^{-1} \times \frac{1\ mol}{6.022 \times 10^{23}\ nuclei}$$
$$= 4.55 \times 10^{-12}\ J = 4.55\ pJ$$

(c) Recall that $\mathbf{1\ eV = 1.602 \times 10^{-19}\ J}$. Using the binding energy computed in part (b):

$$E = 4.55 \times 10^{-12}\ J \times \frac{1\ eV}{1.602 \times 10^{-19}\ J}$$
$$= 2.84 \times 10^{7}\ eV = 28.4\ MeV$$

Exercise 7.1.2

What is the binding energy for the nuclide $\mathbf{^{19}_9F}$ (atomic mass: 18.9984 amu) in MeV per nucleus?

Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the band of stability (also called the belt, zone, or valley of stability). The straight line in Figure **7.1.1** represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

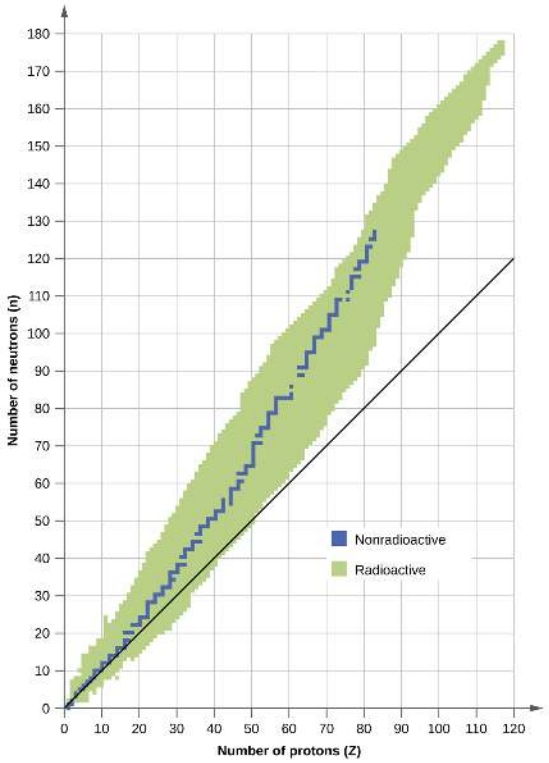


Figure **7.1.1**: This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit radioactivity. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or radioisotope) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (Table **7.1.1**). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as $^{4}_{2}\mathrm{He}$, $^{16}_{8}\mathrm{O}$, $^{40}_{20}\mathrm{Ca}$, and $^{208}_{82}\mathrm{Pb}$ and are particularly stable. These trends in

nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Table 7.1.1: Stable Nuclear Isotopes

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its binding energy per nucleon, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, the binding energy for a $^{4}_{2}\mathrm{He}$ nucleus is therefore:

$$\frac{28.4\ \text{MeV}}{4\ \text{nucleons}} = 7.10\ \text{MeV/nucleon} \tag{7.1.4}$$

The binding energy per nucleon of a nuclide on the curve shown in Figure 7.1.2

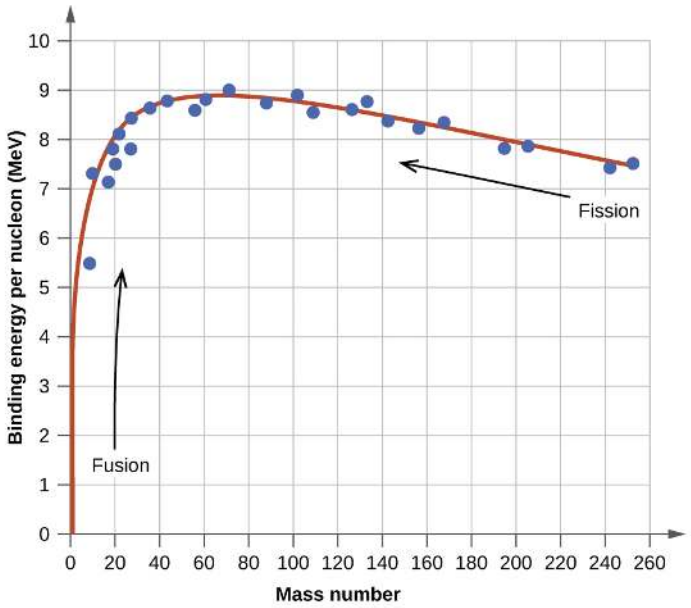


Figure 7.1.2: The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

Example 7.1.3: Calculation of Binding Energy per Nucleon

The iron nuclide $^{56}_{26}\mathrm{Fe}$ lies near the top of the binding energy curve (Figure 7.1.2) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide $^{56}_{26}\mathrm{Fe}$ (atomic mass of 55.9349 amu)?

Solution

As in Example, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an $^{56}_{26}\mathrm{Fe}$ atom:

$$\begin{aligned}\text{Mass defect} &= [(26 \times 1.0073\ \text{amu}) + (30 \times 1.0087\ \text{amu}) + (26 \times 0.00055\ \text{amu})] - 55.9349\ \text{amu} \\ &= 56.4651\ \text{amu} - 55.9349\ \text{amu} \\ &= 0.5302\ \text{amu}\end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$E = mc^2 = 0.5302\ \text{amu} \times \frac{1.6605 \times 10^{-27}\ \text{kg}}{1\ \text{amu}} \times (2.998 \times 10^8\ \text{m/s})^2$$
$$= 7.913 \times 10^{-11}\ \text{kg·m/s}^2$$
$$= 7.913 \times 10^{-11}\ \text{J}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11}\ \text{J} \times \frac{1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} = 493.9\ \text{MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

$$\text{Binding energy per nucleon} = \frac{493.9\ \text{MeV}}{56} = 8.820\ \text{MeV/nucleon}$$

Note that this is almost 25% larger than the binding energy per nucleon for ^4_2He.(Note also that this is the same process as in Example \(\PageIndex{2}\, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

? Exercise 7.1.3

What is the binding energy per nucleon in $^{19}_{9}\text{F}$ (atomic mass, 18.9984 amu)?

Answer

7.810 MeV/nucleon

Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This “missing” mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein’s mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

Key Equations

- $E = mc^2$

Glossary

band of stability
(also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

binding energy per nucleon
total binding energy for the nucleus divided by the number of nucleons in the nucleus

electron volt (eV)
measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

magic number
nuclei with specific numbers of nucleons that are within the band of stability

mass defect

difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

mass-energy equivalence equation

Albert Einstein’s relationship showing that mass and energy are equivalent

nuclear binding energy

energy lost when an atom’s nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry

study of the structure of atomic nuclei and processes that change nuclear structure

nucleon

collective term for protons and neutrons in a nucleus

nuclide

nucleus of a particular isotope

radioactivity

phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radioisotope

isotope that is unstable and undergoes conversion into a different, more stable isotope

strong nuclear force

force of attraction between nucleons that holds a nucleus together

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7.2: Nuclear Equations

Learning Objectives

- Identify common particles and energies involved in nuclear reactions
- Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure **7.2.1**. Protons ($_1^1\mathrm{p}$, also represented by the symbol $_1^1\mathrm{H}$) and neutrons ($_0^1\mathrm{n}$) are the constituents of atomic nuclei, and have been described previously. Alpha particles ($_2^4\mathrm{He}$, also represented by the symbol $_2^4\alpha$) are high-energy helium nuclei. Beta particles ($_{-1}^0\beta$, also represented by the symbol $_{-1}^0\mathrm{e}$) are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. Positrons ($_{+1}^0\mathrm{e}$, also represented by the symbol $_{+1}^0\beta$) are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized $_2^4\mathrm{He}$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.



Figure **7.2.1**: Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

This table has four columns and seven rows. The first row is a header row and it labels each column: "Name," "Symbol(s)," "Representation," and "Description." Under the "Name" column are the following: "Alpha particle," "Beta particle," "Positron," "Proton," "Neutron," and "Gamma ray." Under the "Symbol(s)" column are the following: " superscript 4 stacked over a subscript 2 H e or lowercase alpha," "superscript 0 stacked over a subscript 1 e or lowercase beta," "superscript 0 stacked over a positive subscript 1 e or lowercase beta superscript positive sign," "superscript 1 stacked over a subscript 1 H or lowercase rho superscript 1 stacked over a subscript 1 H," "superscript 1 stacked over a subscript 0 n or lowercase eta superscript 1 stacked over a subscript 0 n," and a lowercase gamma. Under the "Representation column," are the following: two white sphere attached to two blue spheres of about the same size with positive signs in them; a small red sphere with a negative sign in it; a small red sphere with a positive sign in it; a blue spheres with a positive sign in it; a white sphere; and a purple squiggle ling with an arrow pointing right to a lowercase gamma. Under the "Description" column are the following: "(High-energy) helium nuclei consisting of two protons and two neutrons," "(High-energy) elections," "Particles with the same mass as an electron but with 1 unit of positive charge," "Nuclei of hydrogen atoms," "Particles with a mass approximately equal to that of a proton but with no charge," and "Very high-energy electromagnetic radiation."

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of antimatter, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of gamma rays (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$$_{-1}^0\mathrm{e} + {}_{+1}^0\mathrm{e} \rightarrow \gamma + \gamma \tag{7.2.1}$$

Gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays. Gamma rays are produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}\mathrm{O}$ is a product of the nuclear reaction of $^{14}_{7}\mathrm{N}$ and $^{4}_{2}\mathrm{He}$ if we knew that a proton, $^{1}_{1}\mathrm{H}$, was one of the two products. Example 7.2.1 shows how we can identify a nuclide by balancing the nuclear reaction.

Example 7.2.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 ($^{25}_{12}\mathrm{Mg}$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}\mathrm{Mg} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{A}_{Z}\mathrm{X}$$

where

- A is the mass number and
- Z is the atomic number of the new nuclide, X.

Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = \mathrm{A} + 1$$

so

$$\mathrm{A} = 28$$

Similarly, the charges must balance, so:

$$12 + 2 = \mathrm{Z} + 1$$

so

$$\mathrm{Z} = 13$$

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}\mathrm{Al}$.

Exercise 7.2.1

The nuclide $^{125}_{53}\mathrm{I}$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$^{125}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{125}_{52}\mathrm{Te}$$

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\text{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

Summary

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Glossary

alpha particle

(α or $^{4}_{2}\text{He}$ or $^{4}_{2}\alpha$) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter

particles with the same mass but opposite properties (such as charge) of ordinary particles

beta particle

(β or $^{0}_{-1}\text{e}$ or $^{0}_{-1}\beta$) high-energy electron

gamma ray

(γ or $^{0}_{0}\gamma$) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

nuclear reaction

change to a nucleus resulting in changes in the atomic number, mass number, or energy state

positron ($^{0}_{+1}\beta$ or $^{0}_{+1}\text{e}$)

antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

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7.3: Radioactive Decay, Half life, and C-14 Dating

Learning Objectives

- Recognize common modes of radioactive decay
- Identify common particles and energies involved in nuclear decay reactions
- Write and balance nuclear decay equations
- Calculate kinetic parameters for decay processes, including half-life
- Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is radioactive decay. The unstable nuclide is called the parent nuclide; the nuclide that results from the decay is known as the daughter nuclide. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure **7.3.1**).

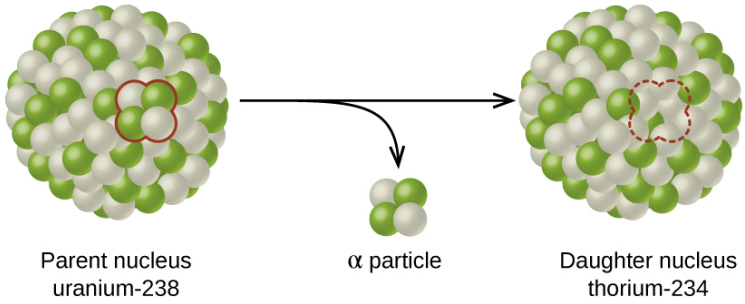


Figure **7.3.1**: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

A diagram shows two spheres composed of many smaller white and green spheres connected by a right-facing arrow with another, down-facing arrow coming off of it. The left sphere, labeled "Parent nucleus uranium dash 238" has two white and two green spheres that are near one another and are outlined in red. These two green and two white spheres are shown near the tip of the down-facing arrow and labeled "alpha particle." The right sphere, labeled "Daughter nucleus radon dash 234," looks the same as the left, but has a space for four smaller spheres outlined with a red dotted line.

Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.



Video 7.3.1: How to Build a Cloud Chamber!

Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 7.3.2) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

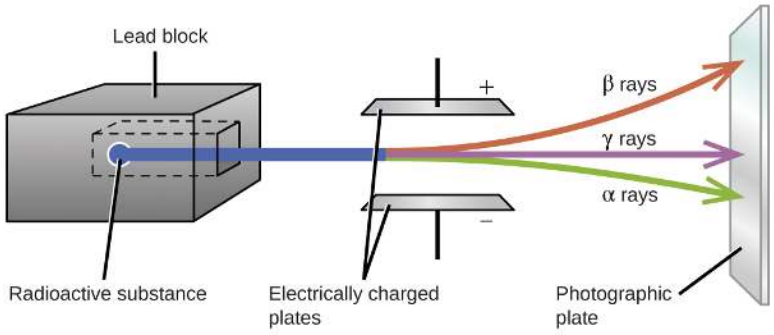


Figure 7.3.2: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

A diagram is shown. A gray box on the left side of the diagram labeled "Lead block" has a chamber hollowed out in the center in which a sample labeled "Radioactive substance" is placed. A blue beam is coming from the sample, out of the block, and passing through two horizontally placed plates that are labeled "Electrically charged plates." The top plate is labeled with a positive sign while the bottom plate is labeled with a negative sign. The beam is shown to break into three beams as it passes in between the plates; in order from top to bottom, they are red, labeled "beta rays," purple labeled "gamma rays" and green labeled "alpha rays." The beams are shown to hit a vertical plate labeled "Photographic plate" on the far right side of the diagram.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\text{He} + {}^{206}_{82}\text{Pb} \quad \text{or} \quad {}^{210}_{84}\text{Po} \longrightarrow {}^{4}_{2}\alpha + {}^{206}_{82}\text{Pb}$$

Alpha decay occurs primarily in heavy nuclei (A > 200, Z > 83). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below **the band of stability**, the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\text{e} + {}^{131}_{54}\text{X} \quad \text{or} \quad {}^{131}_{53}\text{I} \longrightarrow {}^{0}_{-1}\beta + {}^{131}_{54}\text{Xe}$$

Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\mathrm{Co}^{*} \longrightarrow {}^{0}_{0}\gamma + {}^{60}_{27}\mathrm{Co}$$

There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^{+} decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\mathrm{e} + {}^{15}_{7}\mathrm{N} \qquad \text{or} \qquad {}^{15}_{8}\mathrm{O} \longrightarrow {}^{0}_{+1}\beta + {}^{15}_{7}\mathrm{N}$$

Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\mathrm{K} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{40}_{18}\mathrm{Ar}$$

Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur. Figure **7.3.3** summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

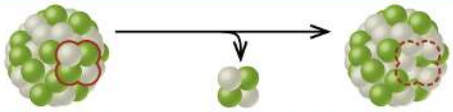
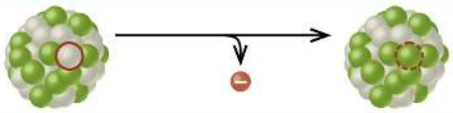
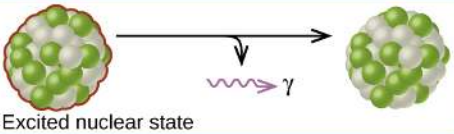
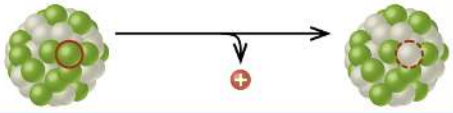
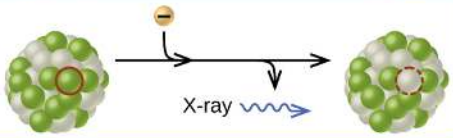
Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

Figure **7.3.3**: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

This table has four columns and six rows. The first row is a header row and it labels each column: “Type,” “Nuclear equation,” “Representation,” and “Change in mass / atomic numbers.” Under the “Type” column are the following: “Alpha decay,” “Beta decay,” “Gamma decay,” “Positron emission,” and “Electron capture.” Under the “Nuclear equation” column are several equations. Each begins with superscript A stacked over subscript Z X. There is a large gap of space and then the following equations: “superscript 4 stacked over subscript 2 He plus superscript A minus 4 stacked over subscript Z minus 2 Y,” “superscript 0 stacked over subscript negative 1 e plus superscript A stacked over subscript Z plus 1 Y,” “superscript 0 stacked over subscript 0 lowercase gamma plus superscript A stacked over subscript Z Y,” “superscript 0 stacked over subscript positive 1 e plus superscript A stacked over subscript Y minus 1 Y,” and “superscript 0 stacked over subscript negative 1 e plus superscript A stacked over subscript Y minus 1 Y.” Under the “Representation” column are the five diagrams. The first shows a cluster of green and white spheres. A section of the cluster containing two white and two green spheres is outlined. There is a right-facing arrow pointing to a similar cluster as previously described, but the outlined section is missing. From the arrow another arrow branches off and points downward. The small cluster to two white spheres and two green spheres appear at the end of the arrow. The next diagram shows the same cluster of white and green spheres. One white sphere is outlined. There is a right-facing arrow to a similar cluster, but the white sphere is missing. Another arrow branches off the main arrow and a red sphere with a negative sign appears at the end. The next diagram shows the same cluster of white and green spheres. The whole sphere is outlined and labeled, “excited nuclear state.” There is a right-facing arrow that points to the same cluster. No spheres are missing. Off the main arrow is another arrow which points to a purple squiggle arrow which in turn points to a lowercase gamma. The next diagram shows the same cluster of white and green spheres. One green sphere is outlined. There is a right-facing arrow to a similar cluster, but the green sphere is missing. Another arrow branches off the main arrow and a red sphere with a positive sign appears at the end. The next diagram shows the same cluster of white and green spheres. One green sphere is outlined. There is a right-facing arrow to a similar cluster, but the green sphere is missing. Two other arrows branch off the main arrow. The first shows a gold sphere with a negative sign joining with the right-facing arrow. The secon points to a blue squiggle arrow labeled, “X-ray.” Under the “Change in mass / atomic numbers” column are the following: “A: decrease by 4, Z: decrease by 2,” “A: unchanged, Z: increased by 1,” “A: unchanged, Z: unchanged,” “A: unchanged, Z: unchanged,” “A: unchanged, Z: decrease by 1,” and “A: unchanged, Z: decrease by 1.”

PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient’s body function (Figure **7.3.4**). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This “tagged” compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.

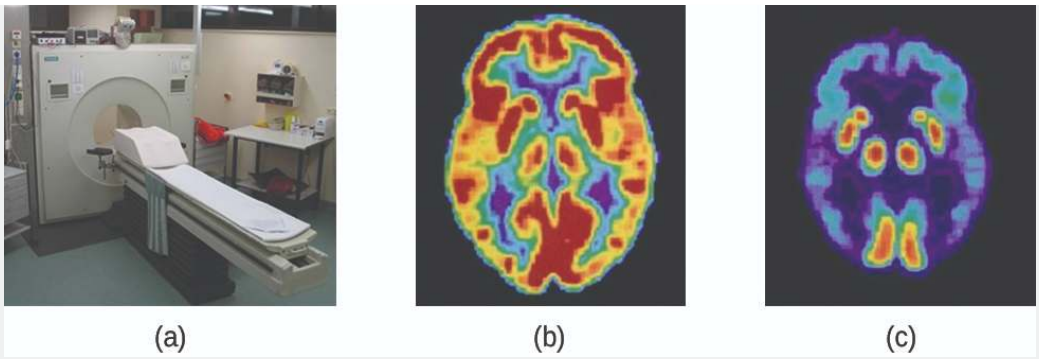


Figure **7.3.4**: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

Three pictures are shown and labeled "a," "b" and "c." Picture a shows a machine with a round opening connected to an examination table. Picture b is a medical scan of the top of a person's head and shows large patches of yellow and red and smaller patches of blue, green and purple highlighting. Picture c also shows a medical scan of the top of a person's head, but this image is mostly colored in blue and purple with very small patches of red and yellow.

For example, F-18 is produced by proton bombardment of ^{18}O ($^{18}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{p} \longrightarrow {}^{18}_{9}\mathrm{F} + {}^{1}_{0}\mathrm{n}$) and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure **7.3.5**). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.

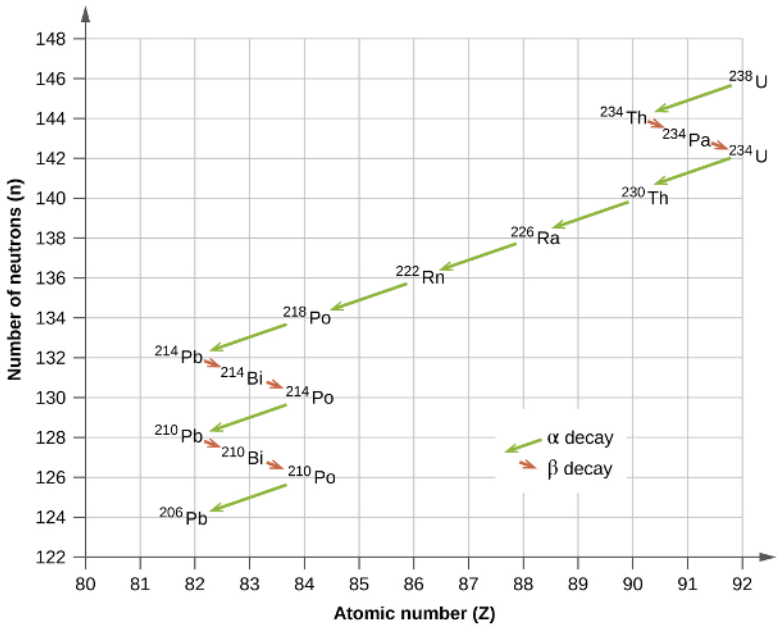


Figure **7.3.5**: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

A graph is shown where the x-axis is labeled “Number of neutrons, open parenthesis, n, close parenthesis” and has values of 122 to 148 in increments of 2. The y-axis is labeled “Atomic number” and has values of 80 to 92 in increments of 1. Two types of arrows are used in this graph to connect the points. Green arrows are labeled as “alpha decay” while red arrows are labeled “beta decay.” Beginning at the point “92, 146” that is labeled “superscript 238, U,” a green arrow connects this point to the second point “90, 144” which is labeled “superscript 234, T h.” A red arrow connect this to the third point “91, 143” which is labeled “superscript 234, P a” which is connected to the fourth point “92, 142” by a red arrow and which is labeled “superscript 234, U.” A green arrow leads to the next point, “90, 140” which is labeled “superscript 230, T h” and is connected by a green arrow to the sixth point, “88, 138” which is labeled “superscript 226, R a” that is in turn connected by a green arrow to the seventh point “86, 136” which is labeled “superscript 222, Ra.” The eighth point, at “84, 134” is labeled “superscript 218, P o” and has green arrows leading to it and away from it to the ninth point “82, 132” which is labeled “superscript 214, Pb” which is connected by a red arrow to the tenth point, “83, 131” which is labeled “superscript 214, B i.” A red arrow leads to the eleventh point “84, 130” which is labeled “superscript 214, P o” and a green arrow leads to the twelvth point “82, 128” which is labeled “superscript 210, P b.” A red arrow leads to the thirteenth point “83, 127” which is labeled “superscript 210, B i” and a red arrow leads to the fourteenth point “84, 126” which is labeled “superscript 210, P o.” The final point is labeled “82, 124” and “superscript 206, P b.”

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope’s half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure **7.3.6**). In a given cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

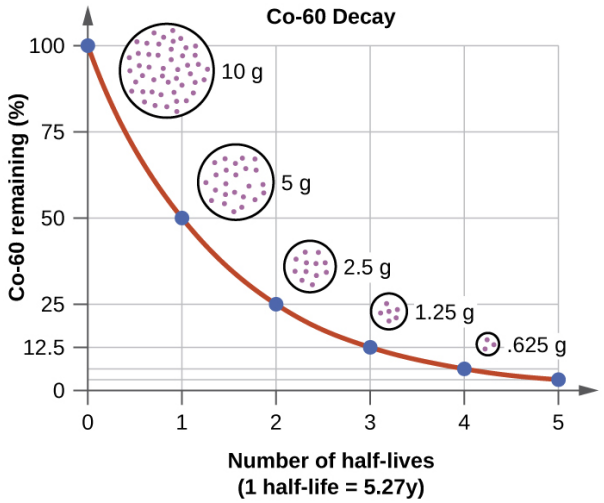


Figure 7.3.6: For cobalt-60, which has a half-life of 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

A graph, titled “C o dash 60 Decay,” is shown where the x-axis is labeled “C o dash 60 remaining, open parenthesis, percent sign, close parenthesis” and has values of 0 to 100 in increments of 25. The y-axis is labeled “Number of half dash lives” and has values of 0 to 5 in increments of 1. The first point, at “0, 100” has a circle filled with tiny dots drawn near it labeled “10 g.” The second point, at “1, 50” has a smaller circle filled with tiny dots drawn near it labeled “5 g.” The third point, at “2, 25” has a small circle filled with tiny dots drawn near it labeled “2.5 g.” The fourth point, at “3, 12.5” has a very small circle filled with tiny dots drawn near it labeled “1.25 g.” The last point, at “4, 6.35” has a tiny circle filled with tiny dots drawn near it labeled.”625 g.”

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the activity of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ is the **decay constant** for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}} \quad \text{or} \quad t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, N, and time are:

$$N_t = N_0 e^{-kt} \quad \text{or} \quad t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

where N_0 is the initial number of nuclei or moles of the isotope, and N_t is the number of nuclei/moles remaining at time t. Example 7.3.1 applies these calculations to find the rates of radioactive decay for specific nuclides.

Example 7.3.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Ni}$.

a. What is the decay constant for the radioactive disintegration of cobalt-60?
b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.
c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27\ \text{y}} = 0.132\ \text{y}^{-1}$$

https://chem.libretexts.org/@go/page/292482

(b) The fraction of $^{60}_{27}\text{Co}$ that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship $N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15.0/\text{y})} = 0.138$$

The fraction of $^{60}_{27}\text{Co}$ that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the $^{60}_{27}\text{Co}$ originally present will remain after 15 years.

(c) 2.00% of the original amount of $^{60}_{27}\text{Co}$ is equal to 0.0200 × N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\ \text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6\ \text{y}$$

? Exercise 7.3.1

Radon-222, $^{222}_{86}\text{Rn}$, has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?

Answer

11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table **7.3.1**, and others are listed in Appendix N1.

Table **7.3.1**: Half-lives of Radioactive Isotopes Important to Medicine

Type	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m[1]	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is radiometric dating and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called radiocarbon dating or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\text{C}$, which constitutes about 99% of the carbon on earth; $^{13}_{6}\text{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\text{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}\text{CO}_2$ to $^{12}_{6}\text{CO}_2$ depends on the ratio of $^{14}_{6}\text{CO}$ to $^{12}_{6}\text{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\text{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\text{C}$ $^{14}_{6}\text{CO}_2$ and $^{12}_{6}\text{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio found in a living plant is the same as the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\text{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + ^{0}_{-1}\text{e}$$

Thus, the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure **7.3.7** visually depicts this process.

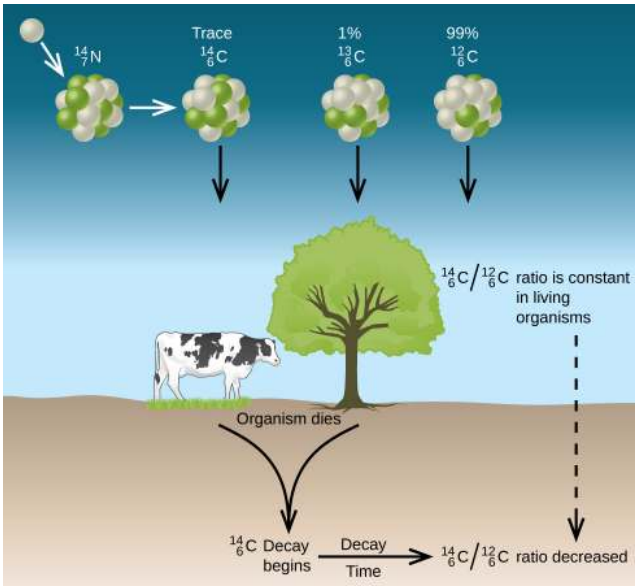


Figure **7.3.7**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

A diagram shows a cow standing on the ground next to a tree. In the upper left of the diagram, where the sky is represented, a single white sphere is shown and is connected by a downward-facing arrow to a larger sphere composed of green and white spheres that is labeled “superscript 14, subscript 7, N.” This structure is connected to three other structures by a right-facing arrow. Each of the three it points to are composed of green and white spheres and all have arrows pointing from them to the ground. The first of these is labeled “Trace, superscript 14, subscript 6, C,” the second is labeled “1 percent, superscript 13, subscript 6, C” and the last is labeled “99 percent, superscript 12, subscript 6, C.” Two downward-facing arrows that merge into one arrow lead from the cow and tree to the ground and are labeled “organism dies” and “superscript 14, subscript 6, C, decay begins.” A right-facing arrow labeled on top as “Decay” and on bottom as “Time” leads from this to a label of “superscript 14, subscript 6, C, backslash, superscript 12, subscript 6, C, ratio decreased.” Near the top of the tree is a downward facing arrow with the label “superscript 14, subscript 6, C, backslash, superscript 12, subscript 6, C, ratio is constant in living organisms” that leads to the last of the lower statements.

For example, with the half-life of $^{14}_{6}\text{C}$ being 5730 years, if the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Example 7.3.2: Radiocarbon Dating

A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.

Solution

The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, *N*, in the relationship:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) \longrightarrow t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right)$$

where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript *t* represents the current time.

The decay constant can be determined from the half-life of C-14, 5730 years:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730\ \text{y}} = 1.21 \times 10^{-4}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{\text{Rate}_t}{\text{Rate}_0}\right) = -\frac{1}{1.21 \times 10^{-4}\ \text{y}^{-1}}\ln\left(\frac{10.8\ \text{dis/min/g C}}{13.6\ \text{dis/min/g C}}\right) = 1910\ \text{y}$$

Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 7.3.8).



Figure 7.3.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

Exercise 7.3.2

More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?

Answer

about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $^{12}_{6}\text{CO}_2$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $^{14}_{6}\text{C}$ has decayed), the ratio of $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ in the atmosphere may be changing. This manmade increase in $^{12}_{6}\text{CO}_2$ in the atmosphere causes the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Example 7.3.3: Radioactive Dating of Rocks

An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.

Solution

The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.

The amount of U-238 currently in the rock is:

$$9.58 \times 10^{-5}\ \cancel{\text{g U}} \times \left(\frac{1\ \text{mol U}}{238\ \cancel{\text{g U}}}\right) = 4.03 \times 10^{-7}\ \text{mol U}$$

Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:

$$2.51 \times 10^{-5}\ \cancel{\text{g Pb}} \times \left(\frac{1\ \cancel{\text{mol Pb}}}{206\ \cancel{\text{g Pb}}}\right) \times \left(\frac{1\ \text{mol U}}{1\ \cancel{\text{mol Pb}}}\right) = 1.22 \times 10^{-7}\ \text{mol U}$$

The total amount of U-238 originally present in the rock is therefore:

$$4.03 \times 10^{-7}\ \text{mol} + 1.22 \times 10^{-7}\ \text{mol} = 5.25 \times 10^{-7}\ \text{mol U}$$

The amount of time that has passed since the formation of the rock is given by:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right)$$

with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.

U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9\ \text{y}} = 1.54 \times 10^{-10}\ \text{y}^{-1}$$

Substituting and solving, we have:

$$t = -\frac{1}{1.54 \times 10^{-10}\ \text{y}^{-1}}\ln\left(\frac{4.03 \times 10^{-7}\ \cancel{\text{mol U}}}{5.25 \times 10^{-7}\ \cancel{\text{mol U}}}\right) = 1.7 \times 10^9\ \text{y}$$

Therefore, the rock is approximately 1.7 billion years old.

Exercise 7.3.3

A sample of rock contains 6.14×10^{-4} g of Rb-87 and 3.51×10^{-5} g of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer

3.7×10^{9} y

Summary

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

Key Equations

- decay rate = λN
- $t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$

Glossary

alpha (α) decay
loss of an alpha particle during radioactive decay

beta (β) decay
breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

daughter nuclide
nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture
combination of a core electron with a proton to yield a neutron within the nucleus

gamma (γ) emission
decay of an excited-state nuclide accompanied by emission of a gamma ray

half-life ($t_{1/2}$)
time required for half of the atoms in a radioactive sample to decay

parent nuclide
unstable nuclide that changes spontaneously into another (daughter) nuclide

positron emission
(also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radioactive decay
spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series

chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radiocarbon dating

highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of $^{14}_{6}\mathrm{C}:\ ^{12}_{6}\mathrm{C}$ in the object vs. the ratio of $^{14}_{6}\mathrm{C}:\ ^{12}_{6}\mathrm{C}$ in the present-day atmosphere

radiometric dating

use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

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7.4: Transmutation and Nuclear Energy

Learning Objectives

- Describe the synthesis of transuranium nuclides
- Explain nuclear fission and fusion processes
- Relate the concepts of critical mass and nuclear chain reactions
- Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

The $^{17}_{8}\text{O}$ and $^{1}_{1}\text{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called particle accelerators are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure **7.4.1**). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure **7.4.1**: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{aligned} {}^{238}_{92}\text{U} + {}^{1}_{0}\text{n} &\longrightarrow {}^{239}_{92}\text{U} \\ {}^{239}_{92}\text{U} &\longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \textbf{half-life} = \textbf{23.5 min} \\ {}^{239}_{93}\text{Np} &\longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \textbf{half-life} = \textbf{2.36 days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \xrightarrow{\beta^-} {}^{239}_{93}\text{Np} \xrightarrow{\beta^-} {}^{239}_{94}\text{Pu}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table **7.4.1**.

Table **7.4.1**: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
einsteinium	Es	99	$^{238}_{92}\text{U} + 15\,{}^{1}_{0}\text{n} \longrightarrow {}^{253}_{99}\text{Es} + 7\,{}^{0}_{-1}\text{e}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4\,{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4\,{}^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3\,{}^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4\,{}^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure **7.4.2**.

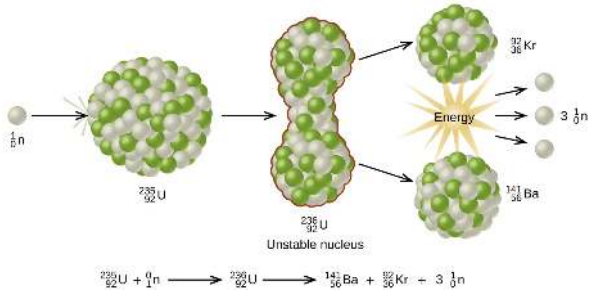


Figure **7.4.2**: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

A diagram is shown which has a white sphere labeled "superscript, 1, subscript 0, n" followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres labeled "superscript, 235, subscript 92, U." The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a vertical dumbbell shaped collection of the same white and green spheres labeled "superscript, 236, subscript 92, U, Unstable nucleus." Two right-facing arrows lead from the top and bottom of this structure to two new spheres that are also composed of green and white spheres and are slightly smaller than the others. The top sphere is labeled "superscript, 92, subscript 36, K r" while the lower one is labeled "superscript, 141, subscript 56, B a." A starburst pattern labeled "Energy" lies between these two spheres and has three right-facing arrows leading from it to three white spheres labeled "3, superscript, 1, subscript 0, n." A balanced nuclear equation is written below the diagram and says "superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 141, subscript 56, B a, plus sign, superscript, 92, subscript 36, K r, plus sign, 3, superscript, 1, subscript 0, n."

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure **7.4.3**. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

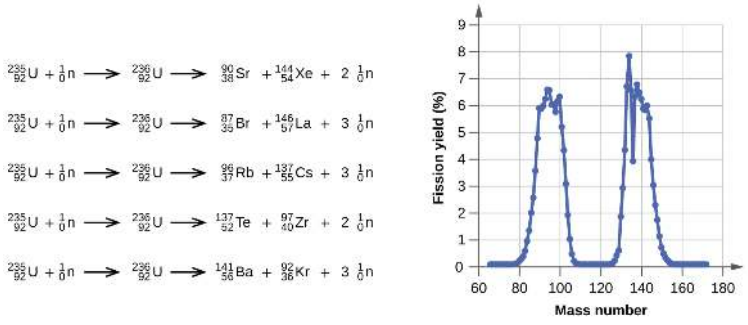


Figure **7.4.3**: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

Five nuclear equations and a graph are shown. The first equation is "superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 90, subscript 38, S r, plus sign, superscript, 144, subscript 54, X e, plus sign, 2, superscript, 1, subscript 0, n." The second equation is "superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 87, subscript 35, B r, plus sign, superscript, 146, subscript 57, L a, plus sign, 3, superscript, 1, subscript 0, n." The third equation is "superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 97, subscript 37, R b, plus sign, superscript, 137, subscript 55, C s, plus sign, 3, superscript, 1, subscript 0, n." The fourth equation is "superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 137, subscript 52, T e, plus sign, superscript, 97, subscript 40, Z r, plus sign, 2, superscript, 1, subscript 0, n." The fifth equation is "superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 236, subscript 92, U, yield arrow, superscript, 141, subscript 56, B a, plus sign, superscript, 92, subscript 36, K r, plus sign, 3, superscript, 1, subscript 0, n." A graph is also shown where the y-axis is labeled "Fission yield, open parenthesis, percent sign, close parenthesis" and has values of 0 to 9 in increments of 1 while the x-axis is labeled "Mass number" and has values of 60 to 180 in increments of 20. The graph begins near point "65, 0" and rises rapidly to near "92, 6.6," then drops just as rapidly to "107, 0" and remains there to point "127, 0." The graph then rises again to near "132, 8," then goes up and down a bit before falling to a point "153, 0," and going horizontal.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical

reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two “medium-sized” nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure **7.4.4**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

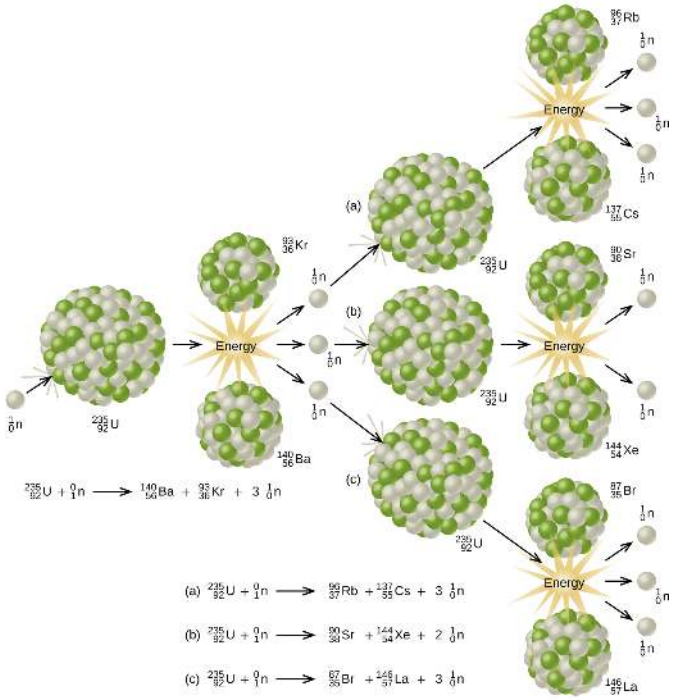


Figure **7.4.4**: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

A diagram is shown which has a white sphere labeled “superscript, 1, subscript 0, n” followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres labeled “superscript, 235, subscript 92, U.” The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. The upper of these two images is labeled “superscript, 93, subscript 36, K r” while the lower of the two is labeled “superscript, 142, subscript 56, B a.” A starburst pattern labeled “Energy” lies between these two spheres and has three right-facing arrows leading from it to three white spheres labeled “ superscript, 1, subscript 0, n.” An equation below this portion of the diagram reads ““superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 140, subscript 56, B a, plus sign, superscript 90, subscript 36, K r, plus sign, 3, superscript 1, subscript 0, n.” A right-facing arrow leads from each of these white spheres to three larger spheres, each composed of many smaller green and white spheres and labeled, from top to bottom as “a, superscript,235, subscript 92, U,” “b, superscript,235, subscript 92, U” and “c, superscript,235, subscript 92, U.” Each of these spheres is followed by a right-facing arrow which points to a pair of smaller spheres composed of the same green and white spheres with starburst patterns in between each pair labeled “Energy.” The spheres of the top pair are labeled, from top to bottom, “superscript, 96, subscript 37, R b” and “superscript, 137, subscript 55, C s.” The spheres of the middle pair are labeled, from top to bottom, “superscript, 90, subscript 38, S r” and “superscript, 144, subscript 54, X e.” The spheres of the bottom pair are labeled, from top to bottom, “superscript, 87, subscript 35, B r” and “superscript, 146, subscript 57, L a.” Each pair of spheres is followed by three right-facing arrows leading to three white spheres labeled “superscript, 1, subscript 0, n.” Below the diagram are three nuclear equations. Equation a reads “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 96, subscript 37, R b, plus sign, superscript 137, subscript 55, C s, plus sign, 3, superscript 1, subscript 0, n.” Equation b reads “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 90, subscript 38, S r, plus sign, superscript144, subscript 54, X e, plus sign, 2, superscript 1, subscript 0, n.” Equation c reads “superscript, 235, subscript 92, U, plus sign, superscript, 1, subscript 0, n, yield arrow, superscript, 87, subscript 35, B r, plus sign, superscript 146, subscript 57, L a, plus sign, 3, superscript 1, subscript 0, n”

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure **7.4.5**).

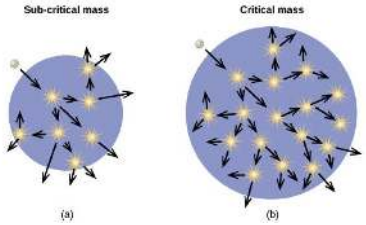


Figure **7.4.5**: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

The images are shown and labeled “a,” “b” and “c.” Image a, labeled “Sub-critical mass,” shows a blue circle background with a white sphere near the outer, top, left edge of the circle. A downward, right-facing arrow indicates that the white sphere enters the circle. Seven small, yellow starbursts are drawn in the blue circle and each has an arrow facing from it to outside the circle, in seemingly random directions. Image b, labeled “Critical mass,” shows a blue circle background with a white sphere near the outer, top, left edge of the circle. A downward, right-facing arrow indicates that the white sphere enters the circle. Seventeen small, yellow starbursts are drawn in the blue circle and each has an arrow facing from it to outside the circle, in seemingly random directions. Image c, labeled “Critical mass from neutron deflection,” shows a blue circle background, lying in a larger purple circle, with a white sphere near the outer, top, left edge of the purple circle. A downward, right-facing arrow indicates that the white sphere enters both of the circles. Thirteen small, yellow starbursts are drawn in the blue circle and each has an arrow facing from it to outside the blue circle, and a couple outside of the purple circle, in seemingly random directions.

An atomic bomb (Figure **7.4.6**) contains several pounds of fissionable material, $^{235}_{92}\mathbf{U}$ or $^{239}_{94}\mathbf{Pu}$, a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.

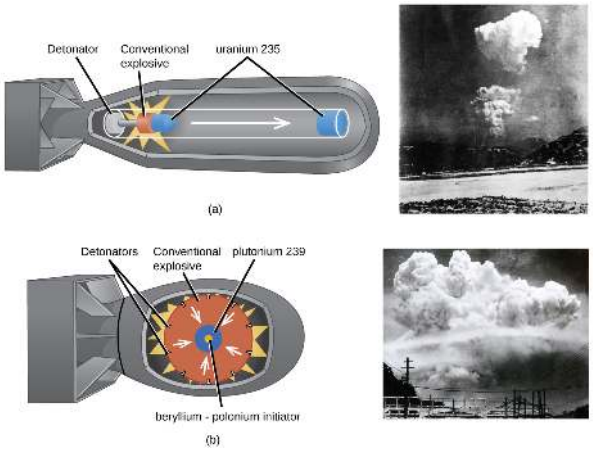


Figure **7.4.6**: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 12, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Two diagrams are shown, each to the left of a photo, and labeled “a” and “b.” Diagram a shows the outer casing of a bomb that has a long, tubular shape with a squared-off tail. Components in the shell show a tube with a white disk labeled “Detonator” on the left, an orange disk with a bright yellow starburst drawn around it labeled “Conventional explosive” in the middle and a right-facing arrow leading to a blue disk in the nose of the bomb labeled “uranium 235.” A small blue cone next to the orange disk is shares the label of “uranium 235.” A black and white photo next to this diagram shows a far-off shot of a rising cloud over a landscape. Diagram b shows the outer casing of a bomb that has a short, rounded shape with a squared-off tail. Components in the shell show a large orange circle labeled “Conventional explosive” with a series of black dots around its edge, labeled “Detonators,” and a yellow starburst behind it. White arrows face from the outer edge of the orange circle to a blue circle in the center with a yellow core. The blue circle is labeled “plutonium 239” while the yellow core is labeled “beryllium, dash, polonium initiator.” A black and white photo next to this diagram shows a far-off shot of a giant rising cloud over a landscape.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a nuclear reactor (Figure **7.4.7**). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.

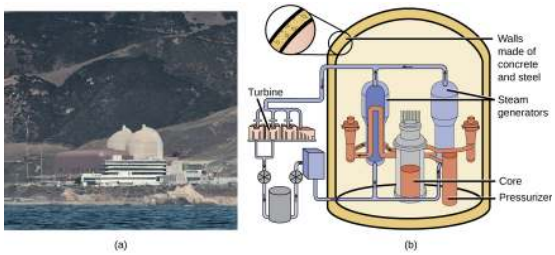


Figure **7.4.7**: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by “Mike” Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

A photo labeled “a” and a diagram labeled “b” is shown. The photo is of a power plant with two large white domes and many buildings. The diagram shows a cylindrical container with thick walls labeled “Walls made of concrete and steel” and three main components inside. The first of these components is a pair of tall cylinders labeled “Steam generators” that sit to either side of a shorter cylinder labeled “Core.” Next to the core is a thin cylinder labeled “Pressurizer.” To the left of the outer walls is a set of pistons labeled “Turbines” that sit above a series of other equipment.

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham’s law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (Figure 21.5.5). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A nuclear moderator is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water ($^2_1H_2O$) or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure **7.4.8**) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\mathrm{B} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.

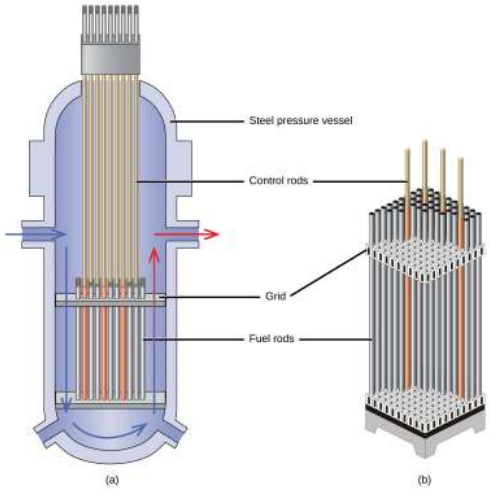


Figure **7.4.8**: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, glossary.periodni.com/glossar...en=control+rod)

Two diagrams are shown and labeled “a” and “b.” Diagram a shows a cut-away view of a vertical tube with a flat, horizontal plate near the bottom that connects to a series of vertical pipes lined up next to one another and labeled “Fuel rods.” A second horizontal plate labeled “Grid” lies at the top of the pipes and a second set of thinner, vertical pipes, labeled “Control rods,” leads from this plate to the top of the container. The walls of the container are labeled “Steel pressure vessel.” A blue, right-facing arrow leads from an entry point in the left side of the container and is followed by a second, down-facing blue arrow and a curved, right-facing arrow that trace along the outer, bottom edge of the container. A blue and red arrow follows these and faces up the right side of the container to an exit near the right face where a red, right-facing arrow leads out. Diagram b is a cut-away image of a vertical, rectangular, three dimensional set of vertical pipes. The pipes are labeled “Fuel rods” and are inserted into an upper and lower horizontal plate labeled “Grid.” Four thin rods extend above the pipes and are labeled “Control rods.

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a containment system (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.



Video **7.4.1**: Click here to watch a 3-minute video from the Nuclear Energy Institute on how nuclear reactors work.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g)$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure **7.4.9**).

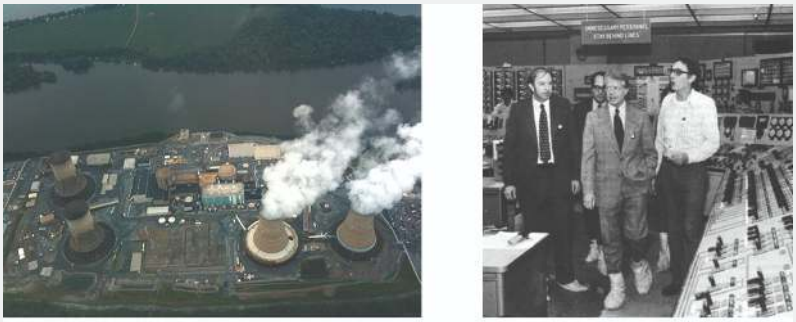


Figure **7.4.9**: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Two photos, labeled “a” and “b” are shown. Photo a is an aerial view of a nuclear power plant. Photo b shows a small group of men walking through a room filled with electronics.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan’s nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan’s atomic energy program is still stalled (Figure **7.4.10**).



Figure **7.4.10**: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by “Live Action Hero”/Flickr)

A photo and a map, labeled “a” and “b,” respectively, are shown. Photo a shows a man in a body-covering safety suit working near a series of blue, plastic coated containers. Map b shows a section of land with the ocean on each side. Near the upper right side of the land is a small red dot, labeled “greater than, 12.5, m R backslash, h r,” that is surrounded by a zone of orange that extends in the upper left direction labeled “2.17, dash, 12.5, m R backslash, h r.” The orange is surrounded by an outline of yellow labeled “1.19, dash, 2.17, m R backslash, h r” and a wider outline of green labeled “0.25, dash, 1.19, m R backslash, h r.” A large area of light blue, labeled “0.03, dash, 0.25, m R backslash, h r” surrounds the green area and extends to the lower middle of the map. A large section of the lower middle and left of the land is covered by dark blue, labeled “less than 0.03, m R backslash, h r.”

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the

fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4{}_1^1\mathrm{H} \longrightarrow {}_2^4\mathrm{He} + 2{}_{+1}^0$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}_2^4\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}_1^2$ and a triton, ${}_1^3$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}_1^2\mathrm{H} + {}_1^3\mathrm{H} \longrightarrow {}_2^4\mathrm{He} + 2{}_0^1\mathrm{n}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^9 kilojoules per mole of ${}_2^4\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure **7.4.11**). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

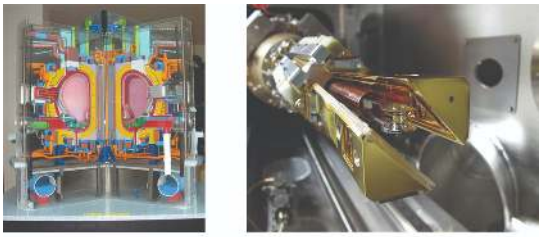


Figure **7.4.11**: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Two photos are shown and labeled "a" and "b." Photo a shows a model of the ITER reactor made up of colorful components. Photo b shows a close-up view of the end of a long, mechanical arm made up of many metal components.

Summary

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

Glossary

chain reaction
repeated fission caused when the neutrons released in fission bombard other atoms

containment system
(also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod
material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass
amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

fissile (or fissionable)
when a material is capable of sustaining a nuclear fission reaction

fission

splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion
combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor
nuclear reactor in which fusion reactions of light nuclei are controlled

nuclear fuel
fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator
substance that slows neutrons to a speed low enough to cause fission

nuclear reactor
environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation
conversion of one nuclide into another nuclide

particle accelerator
device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

reactor coolant
assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

subcritical mass
amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass
amount of material in which there is an increasing rate of fission

transmutation reaction
bombardment of one type of nuclei with other nuclei or neutrons

transuranium element
element with an atomic number greater than 92; these elements do not occur in nature

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7.5: Uses of Radioisotopes

Learning Objectives

- List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

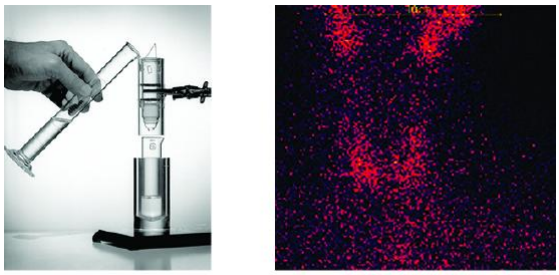
Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure **7.5.1**) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.



Figure **7.5.1**: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

A medical professional is assisting a topless elderly man on a treadmill with sensors and electrical wires connected to his torso.

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure **7.5.2**). The parent nuclide Mo-99 is part of a molybdate ion, $\mathrm{MoO_4^{2-}}$; when it decays, it forms the pertechnetate ion, $\mathrm{TcO_4^-}$. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.



(a) (b)

Figure **7.5.2**: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The MoO_4^{2-} *is retained by the matrix in the column, whereas the* TcO_4^- *passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)*

The first image shows a hand pouring a liquid from a measuring cylinder into a column held up by a clamp. Below the column is a glass tube. The second picture shows red dots on a dark background dispersed everywhere with four spots of heavily concentrated regions.

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure **7.5.3**). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.

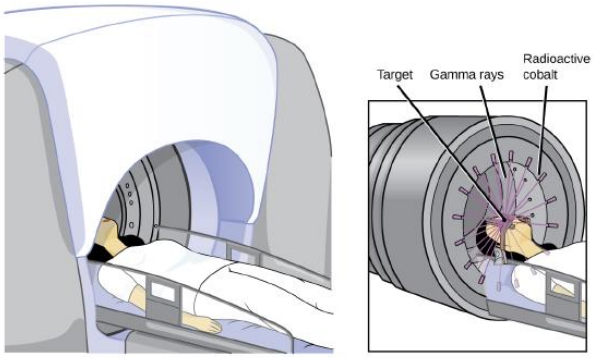


Figure **7.5.3**: The cartoon in (a) shows a cobalt-60 machine used in the treatment of cancer. The diagram in (b) shows how the gantry of the Co-60 machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

A. A woman lies down as she goes into a dome shaped medical machine. B. A closer view of the women's head shows gamma rays from radioactive cobalt attacks the target on the woman's head.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$^{59}_{27}\text{Co} + {}^{1}_{0}\text{n} \longrightarrow {}^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{-1}\beta + 2{}^{0}_{0}\gamma$$

The overall decay scheme for this is shown graphically in Figure **7.5.4**.

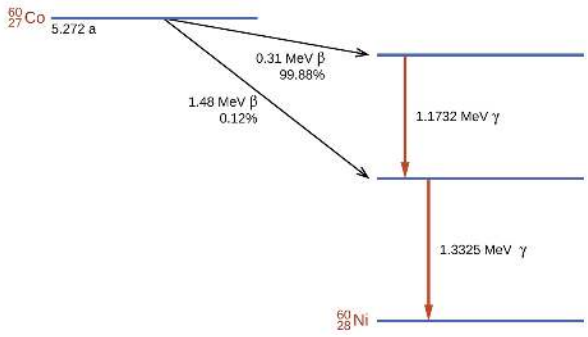


Figure 7.5.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 7.5.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

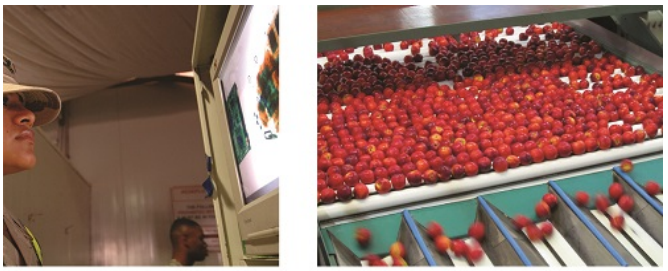


Figure 7.5.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

A. A man is observing a monitor which shows the X-ray of luggages. B. Many apples on processing belts.

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 7.5.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

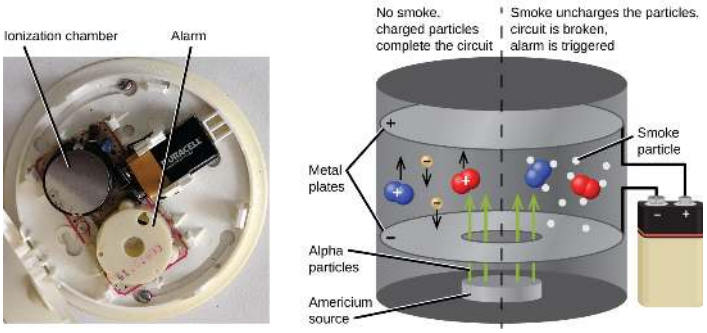


Figure 7.5.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

The inside of a smoke detector is shown with the alarm and ionization chamber labeled. In the picture beside it, a schematic shows the mechanisms of a smoke detector. The two oppositely charged metals plates in the detector are shown along with the Americium source on the bottom part emitting alpha particles. The schematic is divided into two parts, one to show the presence and the other for the absence of smoke.

Summary

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

Glossary

chemotherapy
similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

external beam radiation therapy
radiation delivered by a machine outside the body

internal radiation therapy
(also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

radiation therapy
use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive tracer
(also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

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7.6: Biological Effects of Radiation

Learning Objectives

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure **7.6.1**).

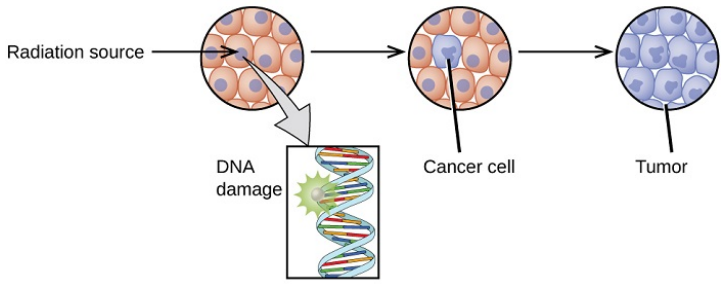


Figure **7.6.1**: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure **7.6.2**).

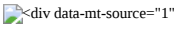


Figure **7.6.2**: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

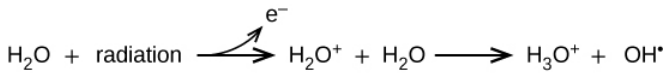


Figure **7.6.3**.

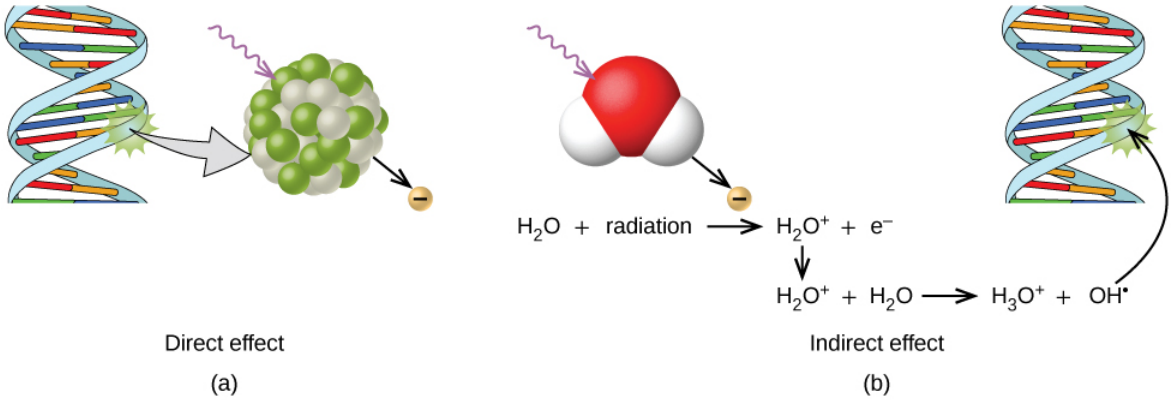


Figure **7.6.3**: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure **7.6.4**). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

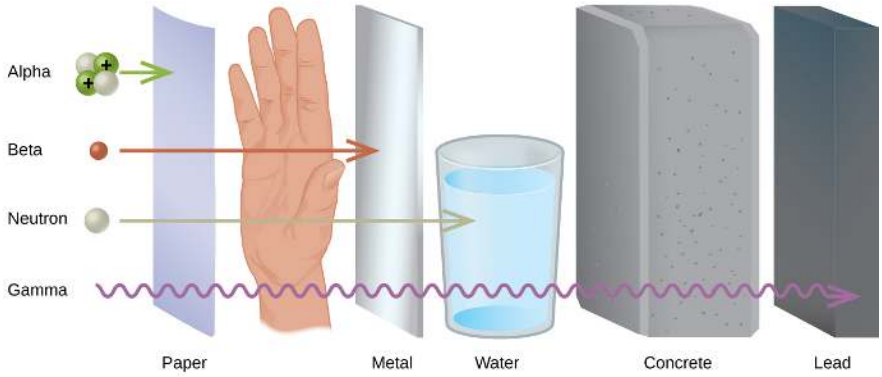


Figure **7.6.4**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person's hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled "Alpha." A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled "Beta" and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled "Neutron" and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, "Paper," "Metal," "Water," "Concrete" and "Lead."

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure **7.6.5**).

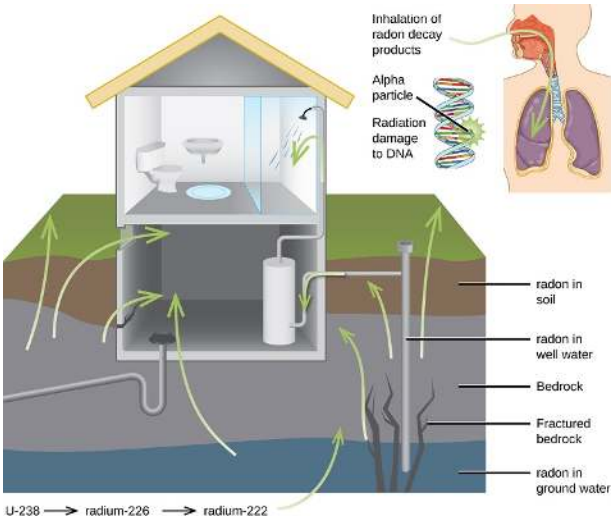


Figure **7.6.5**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of

getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure **7.6.6**). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.



Figure **7.6.6**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

Three photographs are shown and labeled "a," "b" and "c." Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person's hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table **7.6.1**). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = $\mathbf{3.7 \times 10^{10}}$ disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table **7.6.1**: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes $\mathbf{3.7 \times 10^{10}}$ **decays/second**
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor

referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{7.6.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

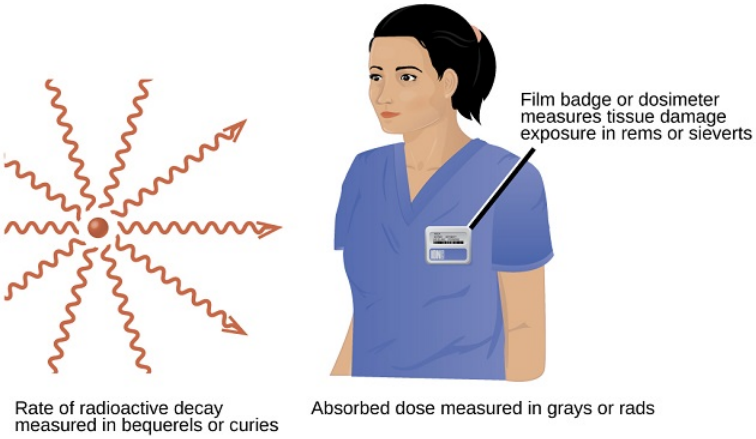


Figure 7.6.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled “Rate of radioactive decay measured in becquerels or curies,” shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads “Film badge or dosimeter measures tissue damage exposure in rems or sieverts” while a phrase under this image states “Absorbed dose measured in grays or rads.”

Example 7.6.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

? Exercise 7.6.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer a

3.56×10^{11} Bq

Answer b

0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 7.6.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

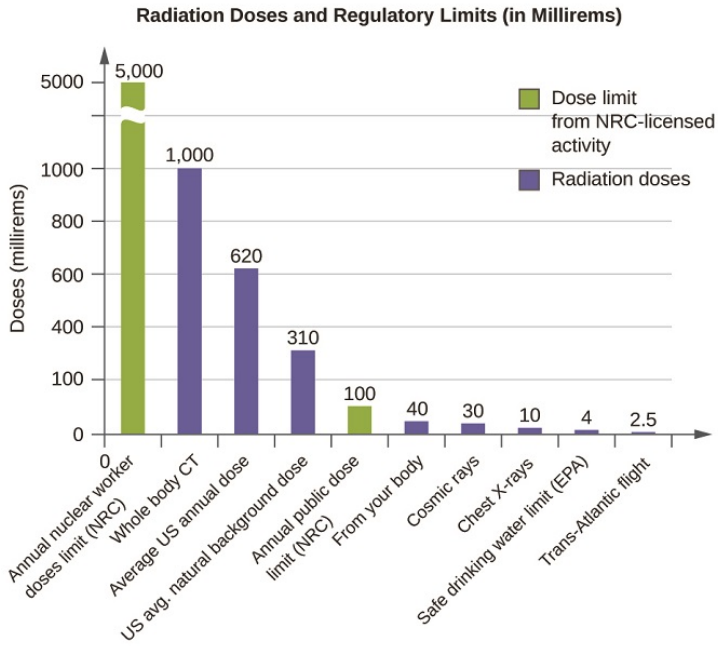


Figure 7.6.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled “Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis” is shown. The y-axis is labeled “Doses in Millirems” and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled “Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis.” The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled “Whole Body C T” while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled “Average U period S period Annual Dose.” The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled “U period S period Natural Background Dose” while the fifth bar, measured to 100 on the y-axis and drawn in red reads “Annual Public Dose Limit, open parenthesis, N R C, close parenthesis.” The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled “From Your Body” while the seventh bar, measured to 30 on the y-axis and drawn in blue reads “Cosmic rays.” The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled “Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis” while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads “Trans Atlantic Flight.” A legend on the graph shows that red means “Dose Limit From N R C dash licensed activity” while blue means “Radiation Doses.”

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table **7.6.2**.

Table **7.6.2**: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)
SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

curie (Ci)
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

Geiger counter
Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

gray (Gy)
SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

ionizing radiation
Radiation that can cause a molecule to lose an electron and form an ion.

millicurie (mCi)
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

nonionizing radiation
Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

radiation absorbed dose (rad)
SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

radiation dosimeter
Device that measures ionizing radiation and is used to determine personal radiation exposure.

relative biological effectiveness (RBE)
Measure of the relative damage done by radiation.

roentgen equivalent man (rem)
Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

scintillation counter
Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

sievert (Sv)
SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

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7.E: Nuclear Chemistry (Practice Problems with Answers)

21.2: Nuclear Structure and Stability

Q21.2.1

Write the following isotopes in hyphenated form (e.g., “carbon-14”)

a. $^{24}_{11}\mathrm{Na}$
b. $^{29}_{13}\mathrm{Al}$
c. $^{73}_{36}\mathrm{Kr}$
d. $^{194}_{77}\mathrm{Ir}$

Q21.2.2

Write the following isotopes in nuclide notation (e.g., " $^{14}_{6}\mathrm{C}$ ")

a. oxygen-14
b. copper-70
c. tantalum-175
d. francium-217

Q21.2.3

For the following isotopes that have missing information, fill in the missing information to complete the notation

a. $^{34}_{14}\mathrm{X}$
b. $_{\mathrm{P}}{}^{36}$
c. $^{57}_{\mathrm{X}}\mathrm{Mn}$
d. $^{121}_{56}\mathrm{X}$

Q21.2.4

For each of the isotopes in Question 21.2.3, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

Q21.2.5

Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

a. 25 protons, 20 neutrons, 24 electrons
b. 45 protons, 24 neutrons, 43 electrons
c. 53 protons, 89 neutrons, 54 electrons
d. 97 protons, 146 neutrons, 97 electrons

Q21.2.6

Calculate the density of the $^{24}_{12}\mathrm{Mg}$ nucleus in g/mL, assuming that it has the typical nuclear diameter of 1×10^{-13} cm and is spherical in shape.

Q21.2.7

What are the two principal differences between nuclear reactions and ordinary chemical changes?

Q21.2.8

The mass of the atom $^{23}_{11}\mathrm{Na}$ is 22.9898 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

Q21.2.9

Which of the following nuclei lie within the band of stability?

a. chlorine-37
b. calcium-40
c. ^{204}Bi
d. ^{56}Fe
e. ^{206}Pb
f. ^{211}Pb
g. ^{222}Rn
h. carbon-14

Q21.2.10

Which of the following nuclei lie within the band of stability?

a. argon-40
b. oxygen-16
c. ^{122}Ba
d. ^{58}Ni
e. ^{205}Tl
f. ^{210}Tl
g. ^{226}Ra
h. magnesium-24

21.3: Nuclear Equations

Q21.3.1

Write a brief description or definition of each of the following:

a. nucleon
b. α particle
c. β particle
d. positron
e. γ ray
f. nuclide
g. mass number
h. atomic number

Q21.3.2

Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

Q21.3.3

Complete each of the following equations by adding the missing species:

a. $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \longrightarrow \ ? + {}^{1}_{0}\mathrm{n}$
b. $^{239}_{94}\mathrm{Pu} + \ ? \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
c. $^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow \ ? + {}^{1}_{1}\mathrm{H}$
d. $^{235}_{92}\mathrm{U} \longrightarrow \ ? + {}^{135}_{55}\mathrm{Cs} + 4{}^{1}_{0}\mathrm{n}$

Q21.3.4

Complete each of the following equations:

a. $^{7}_{3}\mathrm{Li} + \ ? \longrightarrow 2{}^{4}_{2}\mathrm{He}$
b. $^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + \ ?$

c. $^{27}_{13}\mathrm{Al} + {}^{4}_{2}\mathrm{He} \longrightarrow \; ? + {}^{1}_{0}\mathrm{n}$
d. $^{250}_{96}\mathrm{Cm} \longrightarrow \; ? + {}^{98}_{38}\mathrm{Sr} + 4{}^{1}_{0}\mathrm{n}$

Q21.3.5

Write a balanced equation for each of the following nuclear reactions:

a. the production of ^{17}O from ^{14}N by α particle bombardment
b. the production of ^{14}C from ^{14}N by neutron bombardment
c. the production of ^{233}Th from ^{232}Th by neutron bombardment
d. the production of ^{239}U from ^{238}U by $^{2}_{1}\mathrm{H}$ bombardment

Q21.3.6

Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as ^{99}Tc*. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

Q21.3.7

The mass of the atom $^{19}_{9}\mathrm{F}$ is 18.99840 amu.

a. Calculate its binding energy per atom in millions of electron volts.
b. Calculate its binding energy per nucleon.

Q21.3.8

For the reaction $^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + \; ?$, if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273 K and 1 atm?

21.4: Radioactive Decay

Q21.4.1

What are the types of radiation emitted by the nuclei of radioactive elements?

Q21.4.2

What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

a. an α particle is emitted
b. a β particle is emitted
c. γ radiation is emitted
d. a positron is emitted
e. an electron is captured

Q21.4.3

What is the change in the nucleus that results from the following decay scenarios?

a. emission of a β particle
b. emission of a β^{+} particle
c. capture of an electron

Q21.4.4

Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

Q21.4.5

Why is electron capture accompanied by the emission of an X-ray?

Q21.4.6

Explain how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

Q21.4.7

Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

a. chromium-53
b. manganese-51
c. iron-59

Q21.4.8

The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

a. $^{34}_{15}\mathrm{P}$
b. $^{239}_{92}\mathrm{U}$
c. $^{38}_{20}\mathrm{Ca}$
d. $^{3}_{1}\mathrm{H}$
e. $^{245}_{94}\mathrm{Pu}$

Q21.4.9

The following nuclei do not lie in the band of stability. How would they be expected to decay?

a. $^{28}_{15}\mathrm{P}$
b. $^{235}_{92}\mathrm{U}$
c. $^{37}20\mathrm{Ca}$
d. $^{9}_{3}\mathrm{Li}$
e. $^{245}_{96}\mathrm{Cm}$

Q21.4.10

Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

a. $^{6}_{2}\mathrm{He}$
b. $^{60}_{30}\mathrm{Zn}$
c. $^{235}_{91}\mathrm{Pa}$
d. $^{241}_{94}\mathrm{Np}$
e. $^{18}\mathrm{F}$
f. $^{129}\mathrm{Ba}$
g. $^{237}\mathrm{Pu}$

Q21.4.11

Write a nuclear reaction for each step in the formation of $^{218}_{84}\mathrm{Po}$ from $^{238}_{92}\mathrm{U}$, which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α, α particles, in that order.

Q21.4.12

Write a nuclear reaction for each step in the formation of $^{208}_{82}\mathrm{Pb}$ from $^{228}_{90}\mathrm{Th}$, which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

Q21.4.13

Define the term half-life and illustrate it with an example.

Q21.4.14

A 1.00×10^{-6}-g sample of nobelium, $^{254}_{102}\mathrm{No}$, has a half-life of 55 seconds after it is formed. What is the percentage of $^{254}_{102}\mathrm{No}$ remaining at the following times?

a. 5.0 min after it forms
b. 1.0 h after it forms

Q21.4.15

^{239}Pu is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ^{239}Pu present today will be present in 1000 y?

Q21.4.16

The isotope ^{208}Tl undergoes β decay with a half-life of 3.1 min.

a. What isotope is produced by the decay?
b. How long will it take for 99.0% of a sample of pure ^{208}Tl to decay?
c. What percentage of a sample of pure ^{208}Tl remains un-decayed after 1.0 h?

Q21.4.17

If 1.000 g of $^{226}_{88}$Ra produces 0.0001 mL of the gas $^{222}_{86}$Rn at STP (standard temperature and pressure) in 24 h, what is the half-life of ^{226}Ra in years?

Q21.4.18

The isotope $^{90}_{38}$Sr is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

Q21.4.19

Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of $^{99}_{43}$Tc.

Q21.4.20

What is the age of mummified primate skin that contains 8.25% of the original quantity of ^{14}C?

Q21.4.21

A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

a. Calculate the age of the rock if the half-life of the decay of rubidium by β emission is 4.7×10^{10} y.
b. If some $^{87}_{38}$Sr was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

Q21.4.22

A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of $^{238}_{92}$U and 2.52 mg of $^{206}_{82}$Pb. Calculate the age of the ore. The half-life of $^{238}_{92}$U is 4.5×10^9 yr.

Q21.4.23

Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed 4.7×10^9 years ago?

Q21.4.24

A $^{7}_{4}$Be atom (mass = 7.0169 amu) decays into a $^{7}_{3}$Li atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

Q21.4.25

A $^{8}_{5}$B atom (mass = 8.0246 amu) decays into a $^{8}_{4}$Be atom (mass = 8.0053 amu) by loss of a β^+ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

Q21.4.26

Isotopes such as ^{26}Al (half-life: 7.2×10^5 years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

a. ^{26}Al decays by β^+ emission or electron capture. Write the equations for these two nuclear transformations.
b. The earth was formed about 4.7×10^9 (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

Q21.4.27

Write a balanced equation for each of the following nuclear reactions:

a. bismuth-212 decays into polonium-212
b. beryllium-8 and a positron are produced by the decay of an unstable nucleus
c. neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
d. strontium-90 decays into yttrium-90

Q21.4.28

Write a balanced equation for each of the following nuclear reactions:

a. mercury-180 decays into platinum-176
b. zirconium-90 and an electron are produced by the decay of an unstable nucleus
c. thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
d. neon-19 decays into fluorine-19

21.5: Transmutation and Nuclear Energy

Q21.5.1

Write the balanced nuclear equation for the production of the following transuranium elements:

a. berkelium-244, made by the reaction of Am-241 and He-4
b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
c. lawrencium-257, made by the reaction of Cf-250 and B-11
d. dubnium-260, made by the reaction of Cf-249 and N-15

Q21.5.2

How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

Q21.5.3

Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

Q21.5.4

Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

Q21.5.5

Describe the components of a nuclear reactor.

Q21.5.6

In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

Q21.5.7

Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

Q21.5.8

The mass of a hydrogen atom (^1_1H) is 1.007825 amu; that of a tritium atom (^3_1H) is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of ^4_2He produced is released by the following fusion reaction: $^1_1\text{H} + {}^3_1\text{H} \longrightarrow {}^4_2\text{He}$.

21.6: Uses of Radioisotopes

Q21.6.1

How can a radioactive nuclide be used to show that the equilibrium:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \tag{7.E.1}$$

is a dynamic equilibrium?

Q21.6.2

Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

Q21.6.3

Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-131 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β^- emission.

a. Write a nuclear equation for the decay.
b. How long will it take for 95.0% of a dose of I-131 to decay?

21.7: Biological Effects of Radiation

Q21.7.1

If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

a. cobalt-60 (a strong γ emitter used for irradiation)
b. molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

Q21.7.2

Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

Q21.7.3

Given specimens uranium-232 ($t_{1/2} = 68.9\ \text{y}$) and uranium-233 ($t_{1/2} = 159,200\ \text{y}$) of equal mass, which one would have greater activity and why?

Q21.7.4

A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

a. What is its activity in Bq?
b. What is its activity in Ci?

Q21.7.5

Given specimens neon-24 ($t_{1/2} = 3.38\ \text{min}$) and bismuth-211 ($t_{1/2} = 2.14\ \text{min}$) of equal mass, which one would have greater activity and why?

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