CHAPTER 17: EQUILIBRIUM AND EQUILIBRIUM CONSTANTS

Enhanced Introductory College Chemistry

by Gregory Anderson; Caryn Fahey; Jackie MacDonald; Adrienne Richards; Samantha Sullivan Sauer; J.R. van Haarlem; and David Wegman;

Chapter Contents

Except where otherwise noted, this OER is licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/)

Please visit the web version of Enhanced Introductory College Chemistry (https://ecampusontario.pressbooks.pub/enhancedchemistry/) to access the complete book, interactive activities and ancillary resources.

In this chapter, you will learn about

- Chemical reaction rates
- The dynamic nature of a chemical equilibrium
- Equilibrium constants
- The response of a stressed equilibrium using Le Châtelier's Principle
- Equilibrium calculations involving changes to the equilibrium
- Equilibrium constants representing solubility, acids and bases
- Real world examples of equilibria in nature

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Chemical equations
- Reaction stoichiometry
- Molarity
- Solubility
- Reactions of acids and bases

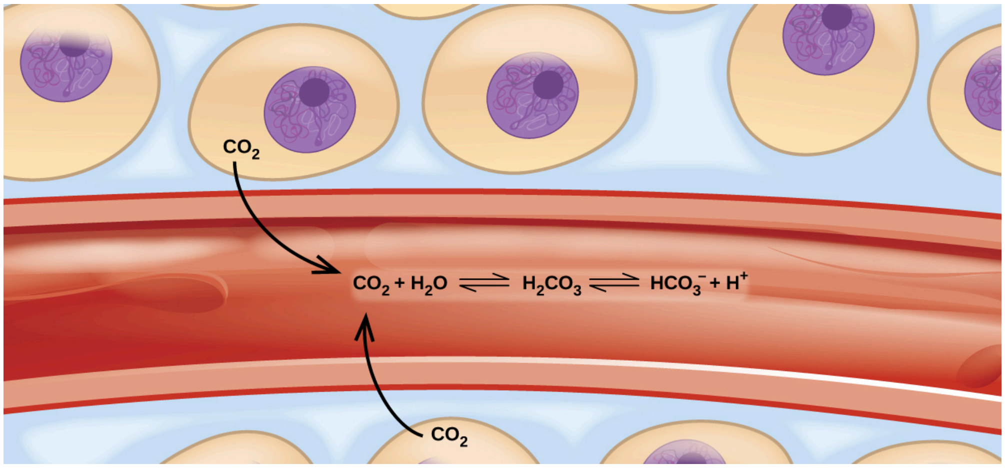


Figure 17a Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (HCO_3^-) (Figure 17.a). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "Chapter 13 Introduction (https://boisestate.pressbooks.pub/chemistry/chapter/intro-13/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

17.1 CHEMICAL REACTION RATES

Learning Objectives

By the end of this section, you will be able to:

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

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

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

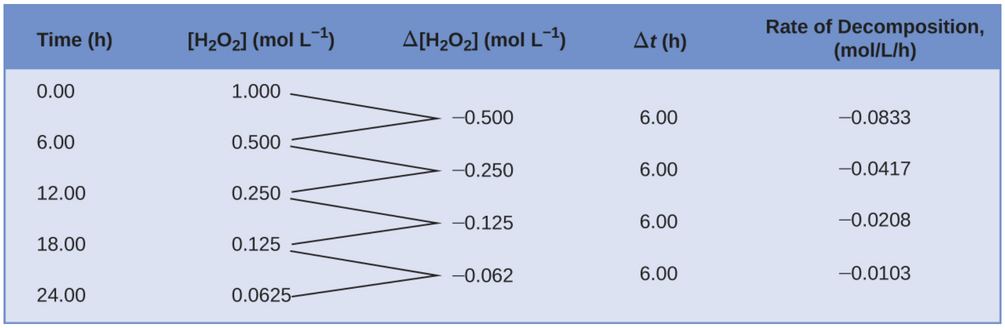
For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according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

$$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) \ + \ \text{O}_2(g)$$

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

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

This mathematical representation of the change in **species (chemical)** concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[H_2O_2]t_1$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]t_2$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure 17.1a provides an example of data collected during the decomposition of H_2O_2.



Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			

Figure 17.1a The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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

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

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

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

This behaviour indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (Figure 17.1b). We can use calculus to evaluate the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

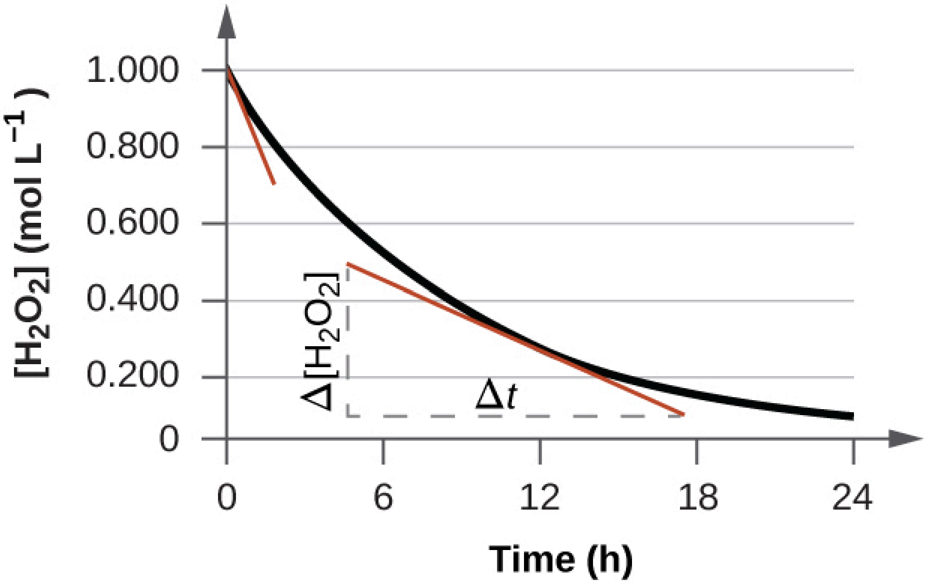


Figure 17.1b This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 10 h ("instantaneous rate" at that particular time) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 17.1c). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in colour upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

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

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

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colourless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct colour change.

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

Figure 17.1c Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: work by J3D3, CC BY-SA 3.0)

Relative Rates of Reaction

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

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

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

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

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

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

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

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

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

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

Figure 17.1d illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at *t* = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

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

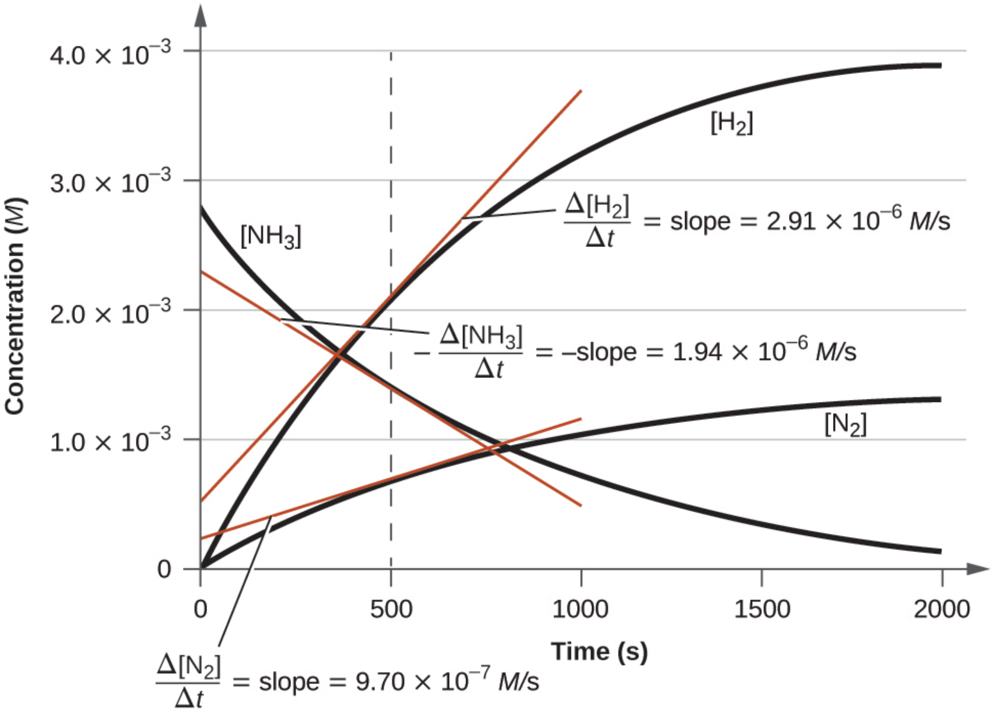


Figure 17.1d This graph shows the changes in concentrations of the reactants and products during the reaction $2NH_3 \rightarrow 3N_2 + H_2$. The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at *t* = 500 s (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 17.1a

Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 17.1b shows the rate of the decomposition of H_2O_2 over time:

$$2\mathrm{H_2O_2} \longrightarrow 2\mathrm{H_2O} + \mathrm{O_2}$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be

3.20×10^{-2} mol/L/h, that is:

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

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

Solution

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

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

Therefore:

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

and

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

Exercise 17.1a

Check Your Learning Exercise (Text Version)

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

a. 5.30×10^{-6} mol/L/s, N_2 and 7.52×10^{-6} mol/L/s, H_2
b. 1.05×10^{-6} mol/L/s, N_2 and 3.15×10^{-6} mol/L/s, H_2

c. 3.15×10^{-6} mol/L/s, N_2 and 1.05×10^{-6} mol/L/s, H_2
d. 2.10×10^{-6} mol/L/s, N_2 and 6.30×10^{-6} mol/L/s, H_2

Check Your Answer[1]

Source: "Exercise 17.1a" is adapted from "Example 12.1-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Key Equations

- relative reaction rates for $a\text{A} \longrightarrow b\text{B} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = \frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t}$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "12.1 Chemical Reaction Rates" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

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

17.2 CHEMICAL EQUILIBRIA

Learning Objectives

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical **equilibrium**, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colourless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

The colour becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Figure 17.2a).

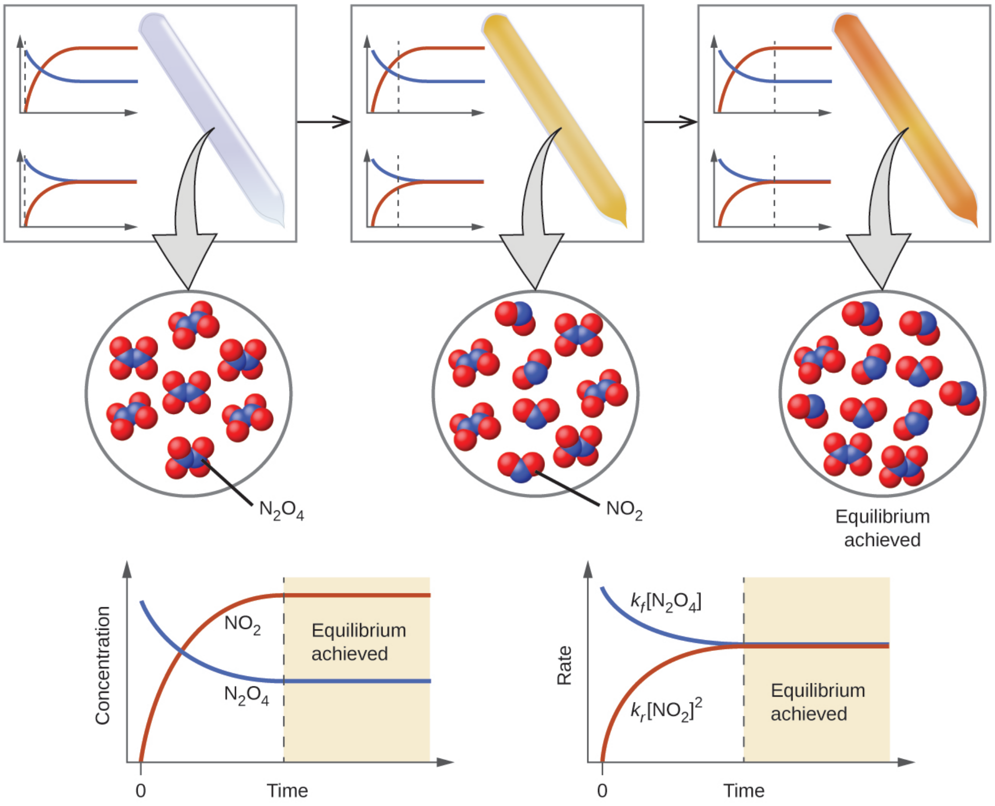


Figure 17.2a A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colourless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the colour of the mixture darkens due to the increasing concentration of NO_2 (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The formation of NO_2 from N_2O_4 is a **reversible reaction**, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure 17.2b).

Figure 17.2b These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant. (credit: work by Cmitasch, CC BY-SA 3.0)

Watch What is chemical equilibrium? (3 mins) (https://youtu.be/dUMmoPdwBy4)

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 17.2a.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 17.2a shows the reaction:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 17.2a, the rate of the forward reaction

$$2\mathrm{NO_2}(g) \longrightarrow \mathrm{N_2O_4}(g)$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4}(g) \longrightarrow 2\mathrm{NO_2}(g)$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$\mathrm{H_2SO_4}(l)\ +\ \mathrm{CaCO_3}(s) \longrightarrow \mathrm{CO_2}(g)\ +\ \mathrm{H_2O}(l)\ +\ \mathrm{CaSO_4}(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions $(\mathrm{HCO_3}^-)$.

$$\mathrm{CO_2}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq)\ +\ \mathrm{H}^+(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles move up out of the beverage, releasing the gas into the air (Figure 17.2c). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as “flat.”

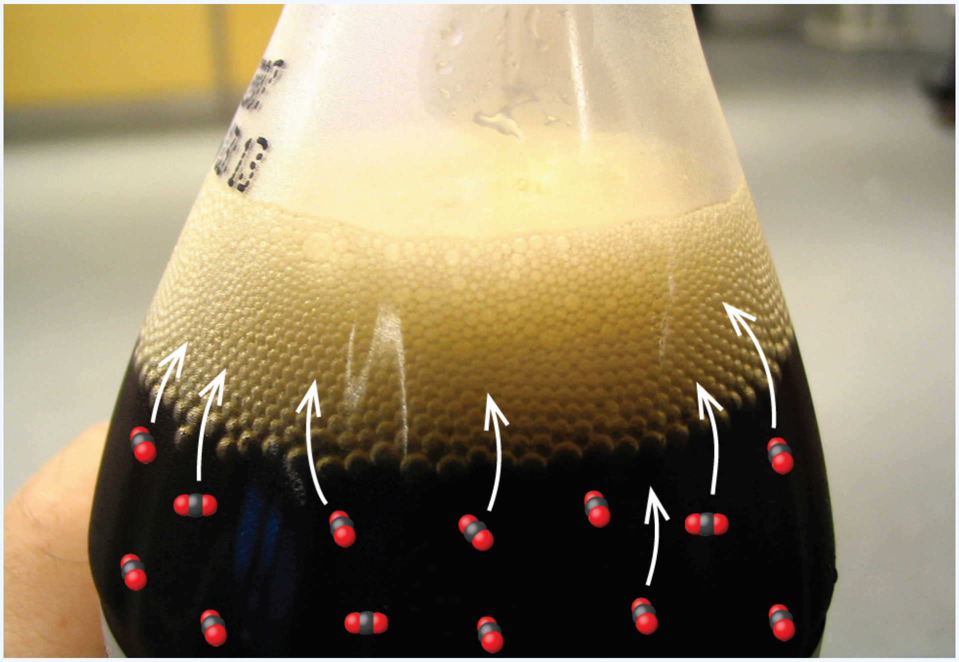


Figure 17.2c When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by Chiara Cotzee, PD; in *Chemistry (OpenStax)*, CC BY 4.0).

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 17.2d shows a sample of liquid bromine at equilibrium with bromine vapour in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapour, some liquid evaporates, the amount of liquid decreases, and the amount of vapour increases. If we cap the bottle so no vapour escapes, the amount of liquid and vapour will eventually stop changing and an equilibrium between the liquid and the vapour will be established. If the bottle were not capped, the bromine vapour would escape and no equilibrium would be reached.

Figure 17.2d An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapour, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapour cannot escape and equilibrium is maintained. (credit: work by Anonymous/Images of Elements, CC BY 3.0)

Exercise 17.2a

Check Your Learning Exercise (Text Version)
True or False? If the concentrations of products and reactants are equal, the system is at equilibrium.

Check Your Answer[1]

Source: "Exercise 17.2a" is adapted from "Exercise 13.1-5" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore Equilibrium Concept from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "13.1 Chemical Equilibria" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

1. False. Equilibrium is reached when the forward and reverse reactions occur at equal rates. The concentrations of products and reactants remain constant.

17.3 EQUILIBRIUM CONSTANTS

Learning Objectives

By the end of this section, you will be able to:

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol ($\rightleftharpoons$) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$$

We can write the **reaction quotient (*Q*)** for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^m[\text{B}]^n}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ is given by this expression:

$$Q_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Example 17.3a

Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3O_2(g) \rightleftharpoons 2O_3(g)$
b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
c. $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

Solution

a. $Q_c = \frac{[O_3]^2}{[O_2]^3}$
b. $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
c. $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Exercise 17.3a

Write the expression for the reaction quotient for each of the following reactions:

a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
b. $C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$
c. $2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$

Check Your Answer[1]

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 17.3a). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

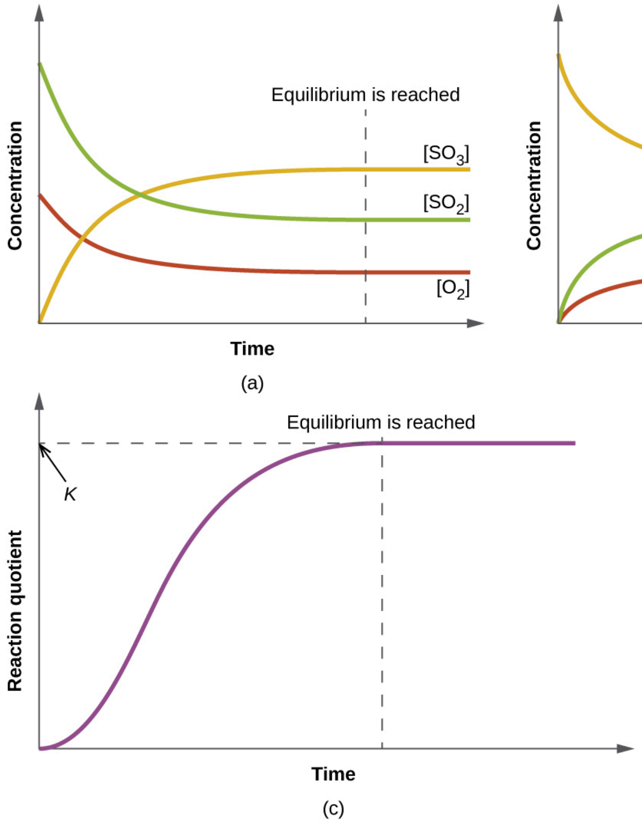


Figure 17.3a (a) The change in the concentrations of reactants and products is depicted as the $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the **equilibrium constant (*K*)** of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y\ldots}{[\mathrm{A}]^m[\mathrm{B}]^n\ldots}$$

This equation is a mathematical statement of the **law of mass action**: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 17.3b

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[NO_2] = 0.016\ M$ and $[N_2O_4] = 0.042\ M$.

a. What is the value of the reaction quotient before any reaction occurs?
b. What is the value of the equilibrium constant for the reaction?

Solution

a. Before any product is formed, $[NO_2] = \frac{0.10\ \text{mol}}{1.0\ \text{L}} = 0.10\ M$, and $[N_2O_4] = 0\ M$. Thus,

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6×10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from concentrations instead of actual concentrations, and so K_c values are truly unitless.

Exercise 17.3b

Check Your Learning Exercise (Text Version)

For the reaction, $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$ the concentrations at equilibrium are $[SO_2]$ = 0.90 *M*, $[O_2]$ = 0.35 *M*, and $[SO_3]$ = 1.1 *M*. What is the value of the equilibrium constant, K_c?

a. 1.1
b. 4.3
c. 8.6
d. 0.90

Check Your Answer[2]

Source: "Exercise 17.3b" is adapted from "Example 13.2-2" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 17.3b illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$\mathrm{CO}(g)\ +\ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g)\ +\ \mathrm{H_2}(g) \qquad K_c = 0.640 \qquad \mathrm{T} = 800\ ^\circ\mathrm{C}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 17.3b when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

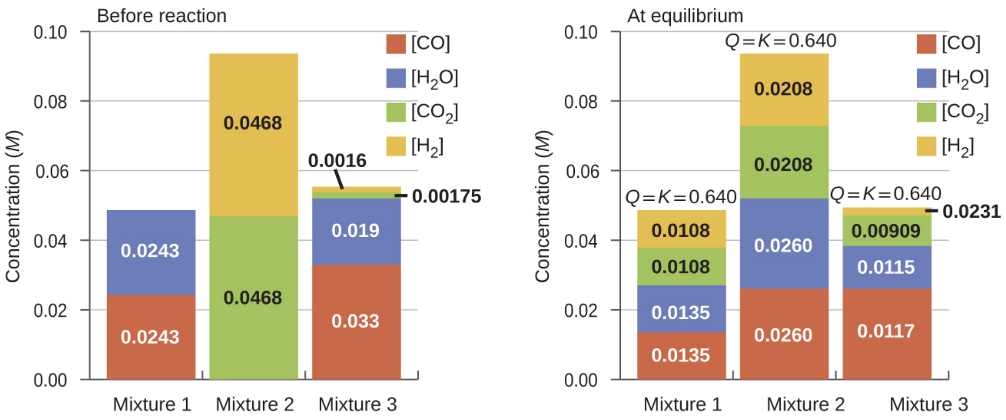


Figure 17.3b Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Example 17.3c

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.0203 M	0.011 M	0.0094 M
$[H_2O]_i$	0.0203 M	0.0011 M	0.0025 M
$[CO_2]_i$	0.0040 M	0.037 M	0.0015 M
$[H_2]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

Exercise 17.3c

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

a. A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl2(g), and 0.500 mol of NOCl:
   $$2\mathrm{NO}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\mathrm{NOCl}(g) \qquad K_c = 4.6 \times 10^4$$
b. A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:
   $$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g) \qquad K_c = 0.060$$
c. A 2.00-L flask containing 230 g of $SO_3(g)$:
   $$2\mathrm{SO_3}(g) \rightleftharpoons 2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \qquad K_c = 0.230$$

Check Your Answer[3]

In Example 17.3c, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (unitless) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a substance’s activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.

As a consequence of this last consideration, Q_c and K_c expressions do not contain terms for solids or liquids (being numerically equal to 1, these terms have no effect on the expression’s value). Several examples of equilibria yielding such expressions will be encountered in this section.

Homogeneous Equilibria

A **homogeneous equilibrium** is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here.

$$\begin{aligned}
\mathrm{C_2H_2}(aq) + 2\mathrm{Br_2}(aq) &\rightleftharpoons \mathrm{C_2H_2Br_4}(aq) & K_c &= \frac{[\mathrm{C_2H_2Br_4}]}{[\mathrm{C_2H_2}][\mathrm{Br_2}]^2} \\
\mathrm{I_2}(aq) + \mathrm{I^-}(aq) &\rightleftharpoons \mathrm{I_3}^-(aq) & K_c &= \frac{[\mathrm{I_3}^-]}{[\mathrm{I_2}][\mathrm{I^-}]} \\
\mathrm{Hg_2}^{2+}(aq) + \mathrm{NO_3}^-(aq) &+ 3\mathrm{H_3O^+}(aq) \\
\rightleftharpoons 2\mathrm{Hg^{2+}}(aq) + \mathrm{HNO_2}(aq) &+ 4\mathrm{H_2O}(l) & K_c &= \frac{[\mathrm{Hg^{2+}}]^2[\mathrm{HNO_2}]}{[\mathrm{Hg_2}^{2+}][\mathrm{NO_3}^-][\mathrm{H_3O^+}]^3} \\
\mathrm{HF}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) & K_c &= \frac{[\mathrm{H_3O^+}][\mathrm{F^-}]}{[\mathrm{HF}]} \\
\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{NH_4}^+(aq) + \mathrm{OH^-}(aq) & K_c &= \frac{[\mathrm{NH_4}^+][\mathrm{OH^-}]}{[\mathrm{NH_3}]}
\end{aligned}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, its concentration does not appear as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well.

$$\begin{aligned} C_2H_6(g) &\rightleftharpoons C_2H_4(g) + H_2(g) & K_c &= \frac{[C_2H_4][H_2]}{[C_2H_6]} \\ 3O_2(g) &\rightleftharpoons 2O_3(g) & K_c &= \frac{[O_3]^2}{[O_2]^3} \\ N_2(g) + 3H_2(g) &\rightleftharpoons 2NH_3(g) & K_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ C_3H_8(g) + 5O_2(g) &\rightleftharpoons 3CO_2(g) + 4H_2O(g) & K_c &= \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5} \end{aligned}$$

Note that the concentration of $H_2O(g)$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where M is the molar concentration of gas, $\frac{n}{V}$.

$$\begin{aligned} PV &= nRT \\ P &= \left(\tfrac{n}{V}\right) RT \\ &= MRT \end{aligned}$$

Thus, at constant temperature, the pressure of a gas is directly proportional to its concentration.

Using the partial pressures of the gases, we can write the reaction quotient for the system $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$ by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{C_2H_6}$ is the partial pressure of C_2H_6; P_{H_2}, the partial pressure of H_2; and $P_{C_2H_6}$, the partial pressure of C_2H_4. At equilibrium:

$$K_P = Q_P = \frac{P_{C_2H_4} P_{H_2}}{P_{C_2H_6}}$$

The subscript P in the symbol $\boldsymbol{K_P}$ designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for $\boldsymbol{K_c}$, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$:

$$\begin{aligned}
K_P &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\
&= \frac{([\text{C}] \times RT)^x ([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m ([\text{B}] \times RT)^n} \\
&= \frac{[\text{C}]^x [\text{D}]^y}{[\text{A}]^m [\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\
&= K_c (RT)^{(x+y) - (m+n)} \\
&= K_c (RT)^{\Delta n}
\end{aligned}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\text{A} + n\text{B} \leftrightharpoons x\text{C} + y\text{D}$, we have

$$\Delta n = (x + y) - (m + n)$$

Example 17.3d

Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\text{C}_2\text{H}_6(g) \rightleftharpoons \text{C}_2\text{H}_4(g) + \text{H}_2(g)$
b. $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$
c. $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:
$\text{CS}_2(g) + 4\text{H}_2(g) \rightleftharpoons \text{CH}_4(g) + 2\text{H}_2\text{S}(g)$

What is K_P at this temperature?

Solution

a. $\Delta n = (2) - (1) = 1$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1 = K_c\,(RT)$

b. $\Delta n = (2) - (2) = 0$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^0 = K_c$

c. $\Delta n = (2) - (1 + 3) = -2$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-2} = \dfrac{K_c}{(RT)^2}$

d. $K_P = K_c\,(RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Exercise 17.3d

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
b. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
c. $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$
d. At 227 °C, the following reaction has $K_c = 0.0952$:
$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$
What would be the value of K_P at this temperature

Check Your Answer[4]

Heterogeneous Equilibria

A **heterogeneous equilibrium** is a system in which reactants and products are found in two or more phases.

The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes; for example:

$$\begin{aligned} \mathrm{PbCl_2}(s) &\rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\mathrm{Cl^-}(aq) & K_c &= [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \\ \mathrm{CaO}(s) + \mathrm{CO_2}(g) &\rightleftharpoons \mathrm{CaCO_3}(s) & K_c &= \frac{1}{[\mathrm{CO_2}]} \\ \mathrm{C}(s) + 2\mathrm{S}(g) &\rightleftharpoons \mathrm{CS_2}(g) & K_c &= \frac{[\mathrm{CS_2}]}{[\mathrm{S}]^2} \end{aligned}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g) \qquad K_c = [\mathrm{Br_2}]$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using partial pressures instead of concentrations. Two examples are:

$$\begin{aligned} \mathrm{CaO}(s) + \mathrm{CO_2}(g) &\rightleftharpoons \mathrm{CaCO_3}(s) & K_P &= \frac{1}{P_{\mathrm{CO_2}}} \\ \mathrm{C}(s) + 2\mathrm{S}(g) &\rightleftharpoons \mathrm{CS_2}(g) & K_P &= \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \end{aligned}$$

Links to Interactive Learning Tools

Explore Equilibrium Constant Expression from the Physics Classroom.

Key Equations

- $Q = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \qquad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n} \qquad \text{where } m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_{\mathrm{P}} = K_{\mathrm{c}}(RT)^{\Delta n}$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from “13.2 Equilibrium Constants” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

1. (a) $Q_c = \frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2[\mathrm{O_2}]}$; (b) $Q_c = \frac{[\mathrm{C_2H_4}]^2}{[\mathrm{C_4H_8}]}$; (c) $Q_c = \frac{[\mathrm{CO_2}]^8[\mathrm{H_2O}]^{10}}{[\mathrm{C_4H_{10}}]^2[\mathrm{O_2}]^{13}}$
2. b) 4.3
3. (a) $Q_c = 6.45 \times 10^3$, shifts right. (b) $Q_c = 0.12$, shifts left. (c) $Q_c = 0$, shifts right
4.
    1. $K_P = K_c (RT)^{-1}$;
    2. $K_P = K_c (RT)$;
    3. $K_P = K_c (RT)$;
    4. 160 or 1.6×10^2

17.4 SHIFTING EQUILIBRIA: LE CHÂTELIER'S PRINCIPLE

Learning Objectives

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier'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). Next we 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 $Q < \mathrm{K}$) or the reactants (if $\mathrm{Q} > K$) until Q returns to the same value as K.

This process is described by **Le Châtelier'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 Châtelier'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.

Effect of Change in Concentration on Equilibrium

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 17.4a 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 Châtelier'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.

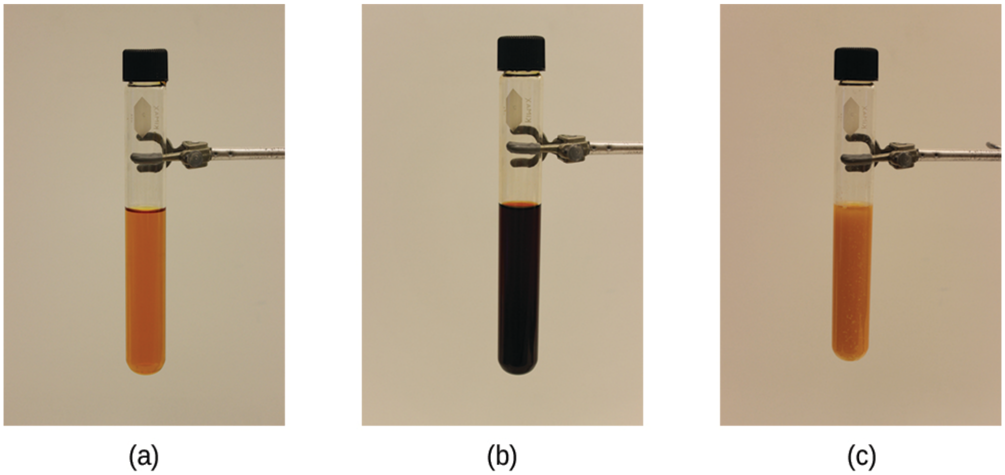


Figure 17.4a (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN^- as the white solid AgSCN. $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN^- concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening colour) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott in *Chemistry (OpenStax)*, CC BY 4.0).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$\mathrm{H_2}(g) \ + \ \mathrm{I_2}(g) \rightleftharpoons \mathrm{2HI}(g) \qquad K_c = 50.0 \text{ at } 400\ ^\circ\mathrm{C}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which $[H_2] = 0.374\ M$, $[I_2] = 0.153\ M$, and $[HI] = 1.692\ M$. This gives:

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI.

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

Check out this video to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Watch Volume Effect on Equilibrium – LeChatelier's Principle Lab Extension (0:43 min)

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 Châtelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favoured because this relieves the stress. The reverse reaction would be favoured by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\mathrm{NO}(g) \;+\; \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favours decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2}(g) \;+\; \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO}(g)$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favour either formation or decomposition of gaseous nitrogen monoxide.

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Châtelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$\mathrm{H_2}(g)\ +\ \mathrm{I_2}(g) \rightleftharpoons 2\mathrm{HI}(g) \qquad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)}$$

Because this reaction is exothermic, we can write it with heat as a product.

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

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, favours the production of heat, and favours the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g) \qquad \Delta H = 57.20\ \mathrm{kJ}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\mathrm{heat}\ +\ \mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

At higher temperatures, the gas mixture has a deep brown colour, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colourless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown colour to fade.

Table 17.4a Effects of Disturbances of Equilibrium and g

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

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

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

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 fibres, and is also used in the steel industry.

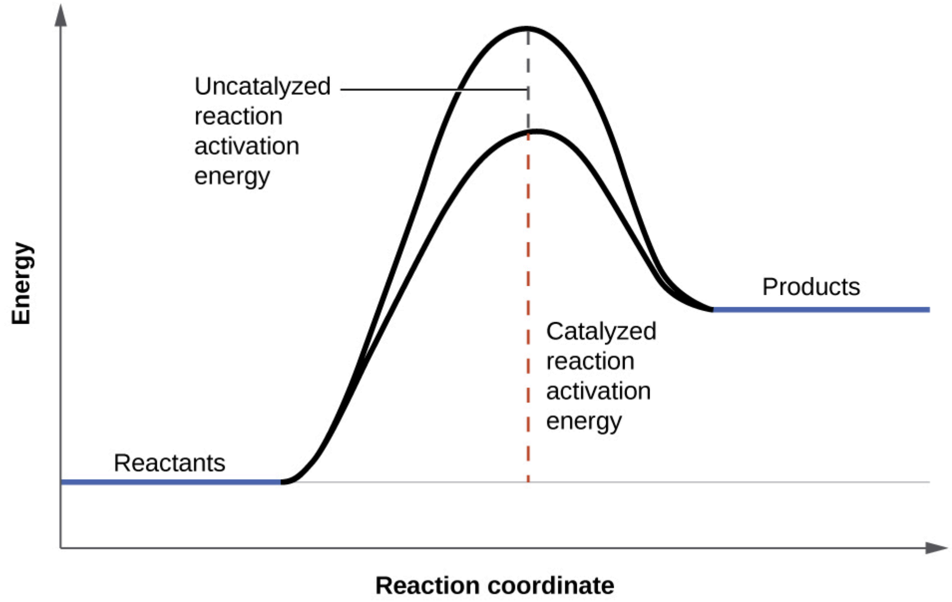


Figure 17.4b The presence of a catalyst increases the rate of a reaction by lowering its activation energy (*General Chemistry 1 & 2*, CC BY 4.0).

Fritz Haber

Figure 17.4c 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. (credit: work by The Nobel Foundation, PD)

In the early 20th century, German chemist Fritz Haber (Figure 17.4c) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient, to ammonia, a form of nitrogen that is easiest for plants to absorb.

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

The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

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. 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. 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.

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.

Indigenous Perspective: The Three Sisters

Also in relation to nitrogen-fixation, a number of Indigenous communities have used another method for nitrogen fixation for hundreds of years. Termed "The Three Sisters", corn, squash and beans are co-planted, and their symbiotic relationship allows for all three plants to produce optimum yields. The corn stalks provide support, giving the bean plants a vertical space to grow upwards. The squash plant's large leaves help maintain soil moisture and can prevent weeds. The bean plants are a natural source of nitrogen-fixation, which helps supports all of the plants. Briefly, the bean plants host the microbe, *rhizobia*, that converts nitrogen from the air into ammonia. This ammonia can then be absorbed by the plant roots.

To learn more about the Three Sisters, **Watch Three Sisters: Companion Planting of North American Indigenous Peoples (10:54 min) (https://youtu.be/UeGRftRk0Uc)**:

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

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

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$\mathrm{N_2}(g)\ +\ 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g) \qquad \Delta H = -92.2\ \mathrm{kJ}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favour the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly.

In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 17.4d).

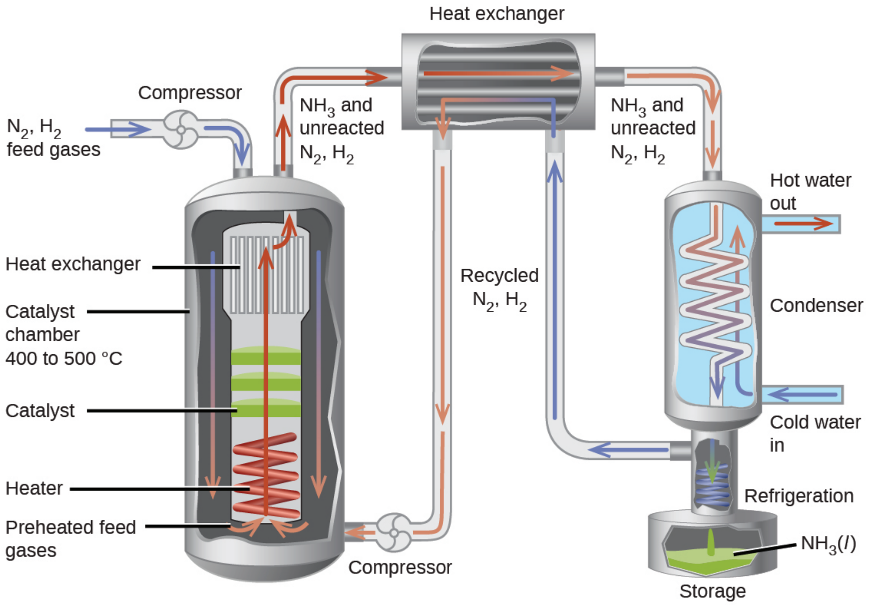


Figure 17.4d Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Exercise 17.4a

Check Your Learning Exercise (Text Version)

Based on the following chemical equation, how can you increase the equilibrium concentration of hydrazine, N_2H_4?

$N_{2(g)} + 2H_{2(g)} \leftrightarrow N_2H_{4(g)}$ $\Delta H = 95$ kJ

a. Add more N_2

b. Add more H_2
c. Increase temperature
d. All of the above

Check Your Answer[2]

Source: "Exercise 17.4a" is adapted from "Exercise 13.3-7" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Links to Interactive Learning Tools

Explore LeChatelier's Principle from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "13.3 Shifting Equilibria: Le Chatelier's Principle" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

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.
2. d) All of the above

17.5 EQUILIBRIUM CALCULATIONS

Learning Objectives

By the end of this section, you will be able to:

- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for Q to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) \ + \ 3\text{H}_2(g)$$

If a sample of ammonia decomposes in a closed system and the concentration of N_2 increases by 0.11 M, the change in the N_2 concentration, $\Delta[\text{N}_2]$, the final concentration minus the initial concentration, is 0.11 M. The change is positive because the concentration of N_2 increases.

The change in the H_2 concentration, $\Delta[\text{H}_2]$, is also positive—the concentration of H_2 increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of H_2 is three times the change in the concentration of N_2 because for each mole of N_2 produced, 3 moles of H_2 are produced.

$$\Delta[\text{H}_2] = 3 \ \times \ \Delta[\text{N}_2]$$

$$= 3 \times (0.11\ M) = 0.33\ M$$

The change in concentration of NH_3, $\Delta[NH_3]$, is twice that of $\Delta[N_2]$; the equation indicates that 2 moles of NH_3 must decompose for each mole of N_2 formed. However, the change in the NH_3 concentration is negative because the concentration of ammonia *decreases* as it decomposes.

$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2 \times (0.11\ M) = -0.22\ M$$

We can relate these relationships directly to the coefficients in the equation:

$$\begin{array}{ccccc} 2\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\mathrm{H_2}(g) \\ \Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] & & \Delta[\mathrm{N_2}] = 0.11\ M & & \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \end{array}$$

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of N_2, we could represent it by the symbol x.

$$\Delta[\mathrm{N_2}] = x$$

The changes in the other concentrations would then be represented as:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$
$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$\begin{array}{ccccc} 2\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\mathrm{H_2}(g) \\ -2x & & x & & 3x \end{array}$$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 17.5a

Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

a. $$\begin{array}{lllllll} C_2H_2(g) & + & 2Br_2(g) & \rightleftharpoons & C_2H_2Br_4(g) \\ x & & \underline{\qquad} & & \underline{\qquad} \end{array}$$

b. $$\begin{array}{lllll} I_2(aq) & + & I^-(aq) & \rightleftharpoons & {I_3}^-(aq) \\ \underline{\qquad} & & \underline{\qquad} & & x \end{array}$$

c. $$\begin{array}{lllllllll} C_3H_8(g) & + & 5O_2(g) & \rightleftharpoons & 3CO_2(g) & + & 4H_2O(g) \\ x & & \underline{\qquad} & & \underline{\qquad} & & \underline{\qquad} \end{array}$$

Solution

a. $$\begin{array}{lllll} C_2H_2(g) & + & 2Br_2(g) & \rightleftharpoons & C_2H_2Br_4(g) \\ x & & 2x & & -x \end{array}$$

b. $$\begin{array}{lllll} I_2(aq) & + & I^-(aq) & \rightleftharpoons & {I_3}^-(aq) \\ -x & & -x & & x \end{array}$$

c. $$\begin{array}{lllllll} C_3H_8(g) & + & 5O_2(g) & \rightleftharpoons & 3CO_2(g) & + & 4H_2O(g) \\ x & & 5x & & -3x & & -4x \end{array}$$

Exercise 17.5a

Complete the changes in concentrations for each of the following reactions:

a.
$$\begin{array}{ccccc} 2\mathrm{SO_2}(g) & + & \mathrm{O_2}(g) & \rightleftharpoons & 2\mathrm{SO_3}(g) \\ \underline{\qquad\quad} & & x & & \underline{\qquad\quad} \end{array}$$

b.
$$\begin{array}{ccc} \mathrm{C_4H_8}(g) & \rightleftharpoons & 2\mathrm{C_2H_4}(g) \\ \underline{\qquad\quad} & & -2x \end{array}$$

c.
$$\begin{array}{ccccccc} 4\mathrm{NH_3}(g) & + & 7\mathrm{H_2O}(g) & \rightleftharpoons & 4\mathrm{NO_2}(g) & + & 6\mathrm{H_2O}(g) \\ \underline{\qquad\quad} & & \underline{\qquad\quad} & & \underline{\qquad\quad} & & \underline{\qquad\quad} \end{array}$$

Check Your Answer[1]

Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant**. If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations**. If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations**. If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_P, K_P, and partial pressure. We will look at solving each of these cases in sequence.

Calculation of an Equilibrium Constant

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE chart—for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the initial concentrations of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the change that occurs as the system shifts toward equilibrium—do not forget to consider the reaction stoichiometry as described in a previous section of this chapter. The last row contains the concentrations once equilibrium has been reached.

Example 17.5b

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

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

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} *M* before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} *M*, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of I_2.

	I_2 +	I^- $\rightleftharpoons$	I_3^-
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x$	$-x$	$+x$
Equilibrium concentration (*M*)	$[1.000 \times 10^{-3}]_i - x$	$[1.000 \times 10^{-3}]_i - x$	x

Since the equilibrium concentration of I_2 is given, we can solve for *x*. At equilibrium the concentration of I_2 is $6.61 \times 10^{-4}\,M$ so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$
$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$
$$= 3.39 \times 10^{-4}\ M$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2 +	I^- $\rightleftharpoons$	I_3^-
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x = -3.39 \times 10^{-4}$	$-x$	$+x$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

We now calculate the value of the equilibrium constant.

$$K_c = Q_c = \frac{[\mathrm{I_3}^-]}{[\mathrm{I_2}][\mathrm{I}^-]}$$
$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

Exercise 17.5b

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odour of some nail polish removers.

$$C_2H_5OH \ + \ CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 \ + \ H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when 0.31 mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Check Your Answer[2]

Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example 17.5c

Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) \ + \ O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, $[N_2]$ = 0.036 mol/L and $[O_2]$ 0.0089 mol/L.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_c = Q_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

$$= \sqrt{(4.1 \ \times \ 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \ \times \ 10^{-7}}$$

$$= 3.6 \ \times \ 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$Q_c = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]}$$

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

$$Q_c = 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

Exercise 17.5c

Check Your Learning Exercise (Text Version)
The equilibrium constant for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

a. 4.26 mol/L
b. 2.09 mol/L
c. 5.45 mol/L
d. 1.53 mol/L

Check Your Answer[3]

Source: “Exercise 17.5c” is adapted from “Example 13.4-3” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Calculation of Changes in Concentration

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
   1. Write a balanced chemical equation for the reaction.
   2. If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
   1. Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol x and express the other changes in terms of the smallest change.
   2. Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
   1. Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for x, and check any assumptions used to find x.
   2. Calculate the equilibrium concentrations.
4. Check the arithmetic.
   1. Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

   Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.
   In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example 17.5d

Calculation of Concentration Changes as a Reaction Goes to Equilibrium

Under certain conditions, the equilibrium constant for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 *M*?

Solution

Use the stepwise process described earlier.

1. *Determine the direction the reaction proceeds.*
   The balanced equation for the decomposition of PCl_5 is
   $$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) \ + \ \mathrm{Cl_2}(g)$$
   Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.
2. *Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.*
   Let us represent the increase in concentration of PCl_3 by the symbol x. The other changes may be written in terms of x by considering the coefficients in the chemical equation.
   $$\begin{array}{ccccc} \mathrm{PCl_5}(g) & \rightleftharpoons & \mathrm{PCl_3}(g) & + & \mathrm{Cl_2}(g) \\ -x & & x & & x \end{array}$$
   The changes in concentration and the expressions for the equilibrium concentrations are:

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	$0 + x = x$	$0 + x = x$

3. *Solve for the change and the equilibrium concentrations.*
   Substituting the equilibrium concentrations into the equilibrium constant equation gives
   $$\begin{aligned} K_c = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} &= 0.0211 \\ &= \frac{(x)(x)}{(1.00 \ - \ x)} \end{aligned}$$
   This equation contains only one variable, x, the change in concentration. We can write the equation as a quadratic equation and solve for x using the quadratic formula.
   $$\begin{gathered} 0.0211 = \frac{(x)(x)}{(1.00 \ - \ x)} \\ 0.0211(1.00 \ - \ x) = x^2 \\ x^2 \ + \ 0.0211x \ - \ 0.0211 = 0 \end{gathered}$$

An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

$$x = \frac{-b \pm \sqrt{b^2 \ - \ 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 \ - \ 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \ \times \ 10^{-4}) \ + \ (8.44 \ \times \ 10^{-2})}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

Hence

$$x = \frac{-0.0211 \ + \ 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 \ - \ 0.291}{2} = -0.156$$

Quadratic equations often have two different solutions, one that is physically possible and one that is physically impossible (an extraneous root). In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, $x = 0.135$ *M*.

The equilibrium concentrations are

$$[\mathrm{PCl_5}] = 1.00 \ - \ 0.135 = 0.87 \ M$$
$$[\mathrm{PCl_3}] = x = 0.135 \ M$$
$$[\mathrm{Cl_2}] = x = 0.135 \ M$$

4. *Check the arithmetic.*
   Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations check.

Exercise 17.5d

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$\mathrm{CH_3CO_2H} + \mathrm{C_2H_5OH} \rightleftharpoons \mathrm{CH_3CO_2C_2H_5} + \mathrm{H_2O}$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 *M* in CH_3CO_2H, 0.15 *M* in C_2H_5OH, 0.40 *M* in $CH_3CO_2C_2H_5$, and 0.40 *M* in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Check Your Answer[4]

Sometimes it is possible to use chemical insight to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products.

Consider the ionization of 0.150 M HA, a weak acid.

$$\mathrm{HA}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{A^-}(aq) \qquad K_c = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the "all reactant" starting point. Using *x* for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	$HA(aq)$ ⇌	$H^+(aq)$ +	$A^-(aq)$
Initial concentration (*M*)	0.150	0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.150 - x$	x	x

Setting up and solving the quadratic equation gives

$$K_c = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(x)(x)}{(0.150 - x)} = 6.80 \times 10^{-4}$$

$$x^2 + (6.80 \times 10^{-4}x) - (1.02 \times 10^{-4}) = 0$$

$$x = \frac{-6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}}{(2)(1)}$$

$$x = 0.00977\ M \text{ or } -0.0104\ M$$

Using the positive (physical) root, the equilibrium concentrations are

$$[\text{HA}] = 0.150 - x = 0.140\ M$$
$$[\text{H}^+] = [\text{A}^-] = x = 0.00977\ M$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the “all product” starting point. Assuming all of the HA ionizes gives

$$[\text{HA}] = 0.150 - 0.150 = 0\ M$$
$$[\text{H}^+] = 0 + 0.150 = 0.150\ M$$
$$[\text{A}^-] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and “*y*” to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	$HA(aq) \rightleftharpoons$	**$H^+(aq)$ +**	**$A^-(aq)$**
Initial concentration (*M*)	0	0.150	0.150
Change (*M*)	$+y$	$-y$	$-y$
Equilibrium concentration (*M*)	y	$0.150 - y$	$0.150 - y$

Setting up and solving the quadratic equation gives

$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.150 - y)(0.150 - y)}{(y)} = 6.80 \times 10^{-4}$$
$$6.80 \times 10^{-4} y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$
$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$
$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$$y = 0.160\ M \qquad \text{or} \qquad y = 0.140\ M$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[\text{HA}] = y = 0.140\ M$$

$$[\mathrm{H}^+] = 0.150 \; - \; y = 0.010 \; M$$
$$[\mathrm{A}^-] = 0.150 \; - \; y = 0.010 \; M$$

Thus, the two approaches give the same results (to three decimal places), and show that both starting points lead to the same equilibrium conditions. The “all reactant” starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the “all product” starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts “close” to equilibrium will require only a ”small” change in conditions (x) to reach equilibrium.

Recall that a small K_c means that very little of the reactants form products and a large K_c means that most of the reactants form products. If the system can be arranged so it starts “close” to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example 17.5e

Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) \; + \; \mathrm{CN}^-(aq) \qquad K_c = 4.9 \; \times \; 10^{-10}$$

Solution

Using “*x*” to represent the concentration of each product at equilibrium gives this ICE table.

	$HCN(aq) \rightleftharpoons$	$H^+(aq)$ +	$CN^-(aq)$
Initial concentration (*M*)	0.15	0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.15 - x$	x	x

The exact solution may be obtained by solving for x in

$$K_c = 4.9 \; \times \; 10^{-10} = \frac{(x)(x)}{0.15 \; - \; x}$$

which, once multiplied through and rearranged, becomes

$$x^2 \; + \; 4.9 \; \times \; 10^{-10} \; - \; 7.35 \; \times \; 10^{-11} = 0$$

Using the quadratic formula with the above, x is determined to be

$$x = 8.5\underline{6} \times 10^{-6}\ M = 8.6 \times 10^{-6}\ M$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6} M$ and [HCN] = 0.15 – *x* = 0.15 *M*.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, *x* must be small compared to 0.15 *M*. More formally, if $x \ll 0.15$, then 0.15 – *x* ≈ 0.15. If this assumption is true, then it simplifies obtaining *x*

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$
$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$
$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$
$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF (0.15 – *x*) ≈ 0.15 *M*, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

The second example requires that the original information be processed a bit, but it still can be solved using a small *x* approximation.

Example 17.5f

Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq) \qquad K_c = 5.0 \times 10^{13}$$

$$K_c = \frac{[\text{Cu(NH}_3)_4{}^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 *M* NH_3 what are the concentrations when the system comes to equilibrium?

Solution

The initial concentration of copper(II) is 0.010 *M*. The equilibrium constant is very large so it would be better to start with as much product as possible because "all products" is much closer to equilibrium than "all reactants." Note that Cu^{2+} is the limiting reactant; if all 0.010 *M* of it reacts to form product the concentrations would be

$$[\text{Cu}^{2+}] = 0.010 - 0.010 = 0\ M$$
$$[\text{Cu(NH}_3)_4{}^{2+}] = 0.010\ M$$
$$[\text{NH}_3] = 1.00 - 4 \times 0.010 = 0.96\ M$$

Using these "shifted" values as initial concentrations with *x* as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \rightleftharpoons$	$Cu(NH_3)_4{}^{2+}(aq)$
Initial concentration (*M*)	0	0.96	0.010
Change (*M*)	$+x$	$+4x$	$-x$
Equilibrium concentration (*M*)	x	$0.96 + 4x$	$0.010 - x$

Since we are starting close to equilibrium, *x* should be small so that

$$0.96 + 4x \approx 0.96\ M$$
$$0.010 - x \approx 0.010\ M$$
$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$
$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[\text{Cu}^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[\text{NH}_3] = 0.96 - 4x = 0.96\ M$$
$$[\text{Cu(NH}_3)_4{}^{2+}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (*x*) was very small. With only a small change required to get to equilibrium, the equation for *x* was greatly simplified and gave a valid result well within the 5% error maximum.

Exercise 17.5e

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 *M* NH_3 solution?

$$\text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni(NH}_3)_6{}^{2+}(aq) \qquad K_c = 5.5 \times 10^8$$

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (*x*) of the product shifts left. Calculate the error in your assumption.

Check Your Answer[5]

Link to Interactive Learning Tools

Explore Equilibrium Calculations from the Physics Classroom.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from “13.4 Equilibrium Calculations” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

1. (a) $2x$, x, $-2x$; (b) x, $-2x$; (c) $4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$
2. $K_c = 5$
3. d) 1.53 mol/L
4. $[CH_3CO_2H] = 0.36\ M$, $[C_2H_5OH] = 0.36\ M$, $[CH_3CO_2C_2H_5] = 0.17\ M$, $[H_2O] = 0.17\ M$
5. $[\text{Ni(NH}_3)_6{}^{2+}] = 0.25\ M$, $[NH_3] = 0.50\ M$, $[Ni^{2+}] = 2.9 \times 10^{-8} M$, error = 1.2×10^{-5}%

17.6 PRECIPITATION AND DISSOLUTION

Learning Objectives

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

The preservation of medical laboratory blood samples, mining of sea water for magnesium, formulation of over-the-counter medicines such as Milk of Magnesia and antacids, and treating the presence of hard water in your home's water supply are just a few of the many tasks that involve controlling the equilibrium between a slightly soluble ionic solid and an aqueous solution of its ions.

In some cases, we want to prevent dissolution from occurring. Tooth decay, for example, occurs when the calcium hydroxylapatite, which has the formula $Ca_5(PO_4)_3(OH)$, in our teeth dissolves. The dissolution process is aided when bacteria in our mouths feast on the sugars in our diets to produce lactic acid, which reacts with the hydroxide ions in the calcium hydroxylapatite. Preventing the dissolution prevents the decay. On the other hand, sometimes we want a substance to dissolve. We want the calcium carbonate in a chewable antacid to dissolve because the CO_3^{2-} ions produced in this process help soothe an upset stomach.

In this section, we will find out how we can control the dissolution of a slightly soluble ionic solid by the application of Le Châtelier's principle. We will also learn how to use the equilibrium constant of the reaction to determine the concentration of ions present in a solution.

The Solubility Product Constant

Silver chloride is what's known as a sparingly soluble ionic solid (Figure 17.6a). Recall from the solubility rules in an earlier chapter that halides of Ag^+ are not normally soluble. However, when we add an excess of solid AgCl to water, it dissolves to a small extent and produces a mixture consisting of a very dilute solution of Ag^+ and $Cl^−$ ions in equilibrium with undissolved silver chloride:

$$\mathrm{AgCl}(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \mathrm{Ag}^{+}(aq) \ + \ \mathrm{Cl}^{-}(aq)$$

This equilibrium, like other equilibria, is dynamic; some of the solid AgCl continues to dissolve, but at the same time, Ag^+ and Cl^- ions in the solution combine to produce an equal amount of the solid. At equilibrium, the opposing processes have equal rates.

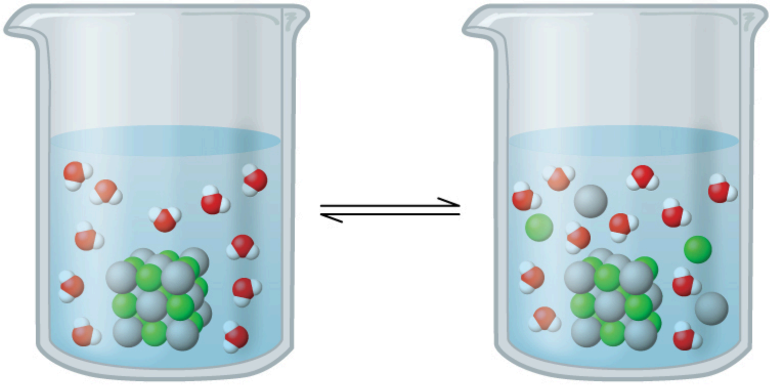


Figure 17.6a Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The equilibrium constant for the equilibrium between a slightly soluble ionic solid and a solution of its ions is called the **solubility product (K_{sp})** of the solid. Recall from the chapter on solutions and colloids that we use an ion's concentration as an approximation of its activity in a dilute solution. For silver chloride, at equilibrium:

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

When looking at dissolution reactions such as this, the solid is listed as a reactant, whereas the ions are listed as products. The solubility product constant, as with every equilibrium constant expression, is written as the product of the concentrations of each of the ions, raised to the power of their stoichiometric coefficients. Here, the solubility product constant is equal to Ag^+ and Cl^- when a solution of silver chloride is in equilibrium with undissolved AgCl. There is no denominator representing the reactants in this equilibrium expression since the reactant is a pure solid; therefore [AgCl] does not appear in the expression for K_{sp}.

Some common solubility products are listed in Table 17.6a according to their K_{sp} values. Each of these equilibrium constants is much smaller than 1 because the compounds listed are only slightly soluble. A small K_{sp} represents a system in which the equilibrium lies to the left, so that relatively few hydrated ions would be present in a saturated solution.

Table 17.6a Common Solubility Products by Decreasing Equilibrium Constants

Substance	K_{sp} at 25 °C
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
AgI	1.5×10^{-16}
PbS	7×10^{-29}
$Al(OH)_3$	2×10^{-32}
$Fe(OH)_3$	4×10^{-38}

Example 17.6a

Writing Equations and Solubility Products

Write the ionic equation for the dissolution and the solubility product expression for each of the following slightly soluble ionic compounds:

a. AgI, silver iodide, a solid with antiseptic properties
b. $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids
c. $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia
d. $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium
e. $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

(Hint: When determining how to break (d) and (e) up into ions, refer to the list of polyatomic ions in the section on chemical nomenclature.)

Solution

a. $\mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{I}^{-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ag}^{+}][\mathrm{I}^{-}]$
b. $\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{CO_3}^{2-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{CO_3}^{2-}]$
c. $\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Mg}^{2+}][\mathrm{OH}^{-}]^2$
d. $\mathrm{Mg(NH_4)PO_4}(s) \rightleftharpoons \mathrm{Mg}^{2+}(aq) + \mathrm{NH_4}^{+}(aq) + \mathrm{PO_4}^{3-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Mg}^{2+}][\mathrm{NH_4}^{+}][\mathrm{PO_4}^{3-}]$
e. $\mathrm{Ca_5(PO_4)3OH}(s) \rightleftharpoons 5\mathrm{Ca}^{2+}(aq) + 3\mathrm{PO_4}^{3-}(aq) + \mathrm{OH}^{-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^5[\mathrm{PO_4}^{3-}]^3[\mathrm{OH}^{-}]$

Exercise 17.6a

Write the ionic equation for the dissolution and the solubility product for each of the following slightly soluble compounds:

a. $BaSO_4$
b. Ag_2SO_4
c. $Al(OH)_3$
d. $Pb(OH)Cl$

Check Your Answer[1]

Now we will extend the discussion of K_{sp} and show how the solubility product constant is determined from the solubility of its ions, as well as how K_{sp} can be used to determine the molar solubility of a substance.

K_{sp} and Solubility

Recall that the definition of *solubility* is the maximum possible concentration of a solute in a solution at a given temperature and pressure. We can determine the solubility product of a slightly soluble solid from that measure of its solubility at a given temperature and pressure, provided that the only significant reaction that occurs when the solid dissolves is its dissociation into solvated ions, that is, the only equilibrium involved is:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{\mathrm{m}+}(aq) \ + \ q\mathrm{X}^{\mathrm{n}\text{-}}(aq)$$

In this case, we calculate the solubility product by taking the solid's solubility expressed in units of moles per litre (mol/L), known as its **molar solubility**.

Example 17.6b

Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF}_2(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) \ + \ 2\mathrm{F}^-(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15 × 10^{-4}*M*; therefore, that of F^{-} is 4.30 × 10^{-4}*M*, that is, twice the concentration of Ca^{2+}. What is the solubility product of fluorite?

Solution

First, write out the K_{sp} expression, then substitute in concentrations and solve for K_{sp}:

$$\mathbf{CaF_2}(s) \rightleftharpoons \mathbf{Ca^{2+}}(aq) \ + \ \mathbf{2F^{-}}(aq)$$

A saturated solution is a solution at equilibrium with the solid. Thus:

$$K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{F}^{-}]^2 = (2.1 \ \times \ 10^{-4})(4.2 \ \times \ 10^{-4})^2 = 3.7 \ \times \ 10^{-11}$$

As with other equilibrium constants, we do not include units with K_{sp}.

Exercise 17.6b

Check Your Learning Exercise (Text Version)
In a saturated solution that is in contact with solid $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31 × 10^{-4}*M*. What is the solubility product for $Mg(OH)_2$?

$MgOH_{2(s)} \leftrightarrow Mg^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$

a. 1.31
b. 4.99×10^{-6}
c. 1.31×10^{-4}
d. 8.99×10^{-12}

Check Your Answer[2]

Source: “Exercise 17.6b” is adapted from “Example 15.1-2” in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 17.6c

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The solubility product constant of copper(I) bromide is 6.3×10^{-9}.

The reaction is:

$$\mathrm{CuBr}(s) \rightleftharpoons \mathrm{Cu}^{+}(aq) + \mathrm{Br}^{-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\mathrm{sp}} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$

Create an ICE table (as introduced in the chapter on fundamental equilibrium concepts), leaving the CuBr column empty as it is a solid and does not contribute to the K_{sp}:

	CuBr $\rightleftharpoons$	Cu^+ +	Br^-
Initial concentration (*M*)		0	0
Change (*M*)		x	x
Equilibrium concentration (*M*)		$0 + x = x$	$0 + x = x$

At equilibrium:

$$K_{\mathrm{sp}} = [\mathrm{Cu}^{+}][\mathrm{Br}^{-}]$$
$$6.3 \times 10^{-9} = (x)(x) = x^2$$
$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}$$

Therefore, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Exercise 17.6c

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Check Your Answer[3]

Example 17.6d

Determination of Molar Solubility from K_{sp}, Part II

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3 × 10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The solubility product constant of calcium hydroxide is 1.3 × 10^{-6}.

The reaction is:

$$\mathrm{Ca(OH)_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) \ + \ 2\mathrm{OH^-}(aq)$$

First, write out the solubility product equilibrium constant expression:

$$K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{OH^-}]^2$$

Create an ICE table, leaving the $Ca(OH)_2$ column empty as it is a solid and does not contribute to the K_{sp}:

	$Ca(OH)_2$ $\rightleftharpoons$	Ca^{2+} +	$2OH^-$
Initial concentration (*M*)		0	0
Change (*M*)		x	$2x$
Equilibrium concentration (*M*)		$0 + x = x$	$0 + 2x = 2x$

At equilibrium:

$$K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{OH^-}]^2$$

$$1.3 \ \times \ 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$

$$x = \sqrt[3]{\frac{1.3 \ \times \ 10^{-6}}{4}} = 6.9 \ \times \ 10^{-3}$$

Therefore, the molar solubility of $Ca(OH)_2$ is 1.3 × 10^{-2} *M*.

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 1.1×10^{-10}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (Figure 17.6b).

Figure 17.6b The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by glitzy queen00, PD)

Further diagnostic testing can be done using barium sulfate and fluoroscopy. In fluoroscopy, a continuous X-ray is passed through the body so the doctor can monitor, on a TV or computer screen, the barium sulfate's movement as it passes through the digestive tract. Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn's disease, and ulcers in addition to other conditions.

Visit Barium X-Rays (Upper and Lower GI) at Johns Hopkins Medicine (https://www.hopkinsmedicine.org/health/conditions-and-diseases/barium-xrays-upper-and-lower-gi) for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) \ + \ \mathrm{CO_3}^{2-}(aq)$$

We can establish this equilibrium either by adding solid calcium carbonate to water or by mixing a solution that contains calcium ions with a solution that contains carbonate ions. If we add calcium carbonate to water, the solid will dissolve until the concentrations are such that the value of the reaction quotient ($Q = [Ca^{2+}][CO_3^{2-}]$) is equal to the solubility product ($K_{sp} = 8.7 \times 10^{-9}$). If we mix a solution of calcium nitrate, which contains Ca^{2+} ions, with a solution of sodium carbonate, which contains CO_3^{2-} ions, the slightly soluble ionic solid $CaCO_3$ will precipitate, provided that the concentrations of Ca^{2+} and CO_3^{2-} ions are such that Q is greater than K_{sp} for the mixture. The reaction shifts to the left and the concentrations of the ions are reduced by formation of the solid until the value of Q equals K_{sp}. A saturated solution in equilibrium with the undissolved solid will result. If the concentrations are such that Q is less than K_{sp}, then the solution is not saturated and no precipitate will form.

We can compare numerical values of Q with K_{sp} to predict whether precipitation will occur, as Example 5 shows. (Note: Since all forms of equilibrium constants are temperature dependent, we will assume a room temperature environment going forward in this chapter unless a different temperature value is explicitly specified.)

Example 17.6e

Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\mathrm{Mg(OH)_2}(s) \rightleftharpoons \mathrm{Mg}^{2+}(aq) \ + \ 2\mathrm{OH}^-(aq) \qquad K_{\mathrm{sp}} = 8.9 \ \times \ 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

This problem asks whether the reaction:

$$\mathrm{Mg(OH)_2}(s) \leftrightharpoons \mathrm{Mg}^{2+}(aq) + 2\mathrm{OH}^-(aq)$$

shifts to the left and forms solid $Mg(OH)_2$ when $[Mg^{2+}]$ = 0.0537 *M* and $[OH^-]$ = 0.0010 *M*. The reaction shifts to the left if Q is greater than K_{sp}. Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\mathrm{Mg}^{2+}][\mathrm{OH}^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), we can expect the reaction to shift to the left and form solid magnesium hydroxide. $Mg(OH)_2(s)$ forms until the concentrations of magnesium ion and hydroxide ion are reduced sufficiently so that the value of Q is equal to K_{sp}.

Example 17.6f

Precipitation of AgCl upon Mixing Solutions

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}–*M* solution of $AgNO_3$ and a 2.0×10^{-4}–*M* solution of NaCl are mixed?

(Note: The solution also contains Na^+ and NO_3^- ions, but when referring to solubility rules, one can see that sodium nitrate is very soluble and cannot form a precipitate.)

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

The solubility product is 1.6×10^{-10} (see Appendix K).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. The volume doubles when we mix equal volumes of $AgNO_3$ and NaCl solutions, so each concentration is reduced to half its initial value. Consequently, immediately upon mixing, $[Ag^+]$ and $[Cl^-]$ are both equal to:

$$\frac{1}{2}(2.0\ \times\ 10^{-4})\ M = 1.0\ \times\ 10^{-4}\ M$$

The reaction quotient, Q, is *momentarily* greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\mathrm{Ag}^{+}][\mathrm{Cl}^{-}] = (1.0\ \times\ 10^{-4})(1.0\ \times\ 10^{-4}) = 1.0\ \times\ 10^{-8} \geq K_{\mathrm{sp}}$$

Since supersaturated solutions are unstable, AgCl will precipitate from the mixture until the solution returns to equilibrium, with Q equal to K_{sp}.

Exercise 17.6d

Will $KClO_4$ precipitate when 20 mL of a 0.050-*M* solution of K^+ is added to 80 mL of a 0.50-*M* solution of ClO_4^-? (Remember to calculate the new concentration of each ion after mixing the solutions before plugging into the reaction quotient expression.)

Check Your Answer[4]

In the previous two examples, we have seen that $Mg(OH)_2$ or AgCl precipitate when Q is greater than K_{sp}. In general, when a solution of a soluble salt of the M^{m+} ion is mixed with a solution of a soluble salt of the X^{n-} ion, the solid, M_pX_q precipitates if the value of Q for the mixture of M^{m+} and X^{n-} is greater than K_{sp} for M_pX_q. Thus, if we know the concentration of one of the ions of a slightly soluble ionic solid and the value for the solubility product of the solid, then we can calculate the concentration that the other ion must exceed for precipitation to begin. To simplify the calculation, we will assume that precipitation begins when the reaction quotient becomes equal to the solubility product constant.

Example 17.6g

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4^{2-}$, for this purpose (Figure 17.6c). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4{\cdot}H_2O$ (which also contains water bound in the solid). The concentration of Ca^{2+} in a sample of blood serum is $2.2 \times 10^{-3} M$. What concentration of $C_2O_4^{2-}$ ion must be established before $CaC_2O_4{\cdot}H_2O$ begins to precipitate?

Figure 17.6c Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind, CC BY 2.0)

Solution

The equilibrium expression is:

$$\mathrm{CaC_2O_4}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) \;+\; \mathrm{C_2O_4{}^{2-}}(aq)$$

For this reaction:

$$K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4{}^{2-}}] = 1.96 \;\times\; 10^{-8}$$

(see Appendix K)

CaC_2O_4 does not appear in this expression because it is a solid. Water does not appear because it is the solvent.

Solid CaC_2O_4 does not begin to form until Q equals K_{sp}. Because we know K_{sp} and $[Ca^{2+}]$, we can solve for the concentration of $C_2O_4^{2-}$ that is necessary to produce the first trace of solid:

$$Q = K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}][\mathrm{C_2O_4{}^{2-}}] = 1.96 \;\times\; 10^{-8}$$

$$(2.2 \times 10^{-3})[C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$
$$[C_2O_4{}^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}$$

A concentration of $C_2O_4{}^{2-}$ = 8.9 × 10^{-6} *M* is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Exercise 17.6e

If a solution contains 0.0020 mol of $CrO_4{}^{2-}$ per litre, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Check Your Answer[5]

It is sometimes useful to know the concentration of an ion that remains in solution after precipitation. We can use the solubility product for this calculation too: If we know the value of K_{sp} and the concentration of one ion in solution, we can calculate the concentration of the second ion remaining in solution. The calculation is of the same type as that in Example 17.6g—calculation of the concentration of a species in an equilibrium mixture from the concentrations of the other species and the equilibrium constant. However, the concentrations are different; we are calculating concentrations after precipitation is complete, rather than at the start of precipitation.

Example 17.6h

Concentrations Following Precipitation

Clothing washed in water that has a manganese [Mn^{2+}(*aq*)] concentration exceeding 0.1 mg/L (1.8 × 10^{-6} *M*) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be reduced by adding a base. If a person doing laundry wishes to add a buffer to keep the pH high enough to precipitate the manganese as the hydroxide, $Mn(OH)_2$, what pH is required to keep [Mn^{2+}] equal to 1.8 × 10^{-6} *M*?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn^{2+}}(aq) \ + \ 2\mathrm{OH^-}(aq) \qquad K_{\mathrm{sp}} = 2 \ \times \ 10^{-3}$$

We need to calculate the concentration of OH^- when the concentration of Mn^{2+} is 1.8×10^{-6} *M*. From that, we calculate the pH. At equilibrium:

$$K_{\mathrm{sp}} = [\mathrm{Mn^{2+}}][\mathrm{OH^-}]^2$$

or

$$(1.8 \ \times \ 10^{-6})[\mathrm{OH^-}]^2 = 2 \ \times \ 10^{-3}$$

so

$$[\mathrm{OH^-}] = 3.3 \ \times \ 10^{-4} \ M$$

Now we calculate the pH from the pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(3.3 \ \times \ 10 \ - \ 4) = 3.48$$
$$\mathrm{pH} = 14.00 \ - \ \mathrm{pOH} = 14.00 \ - \ 3.80 = 10.52$$

If the person doing laundry adds a base, such as the sodium silicate (Na_4SiO_4) in some detergents, to the wash water until the pH is raised to 10.52, the manganese ion will be reduced to a concentration of 1.8×10^{-6} *M*; at that concentration or less, the ion will not stain clothing.

Exercise 17.6f

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which $[Mg^{2+}]$ is diminished to 1.0×10^{-5} *M* by the addition of $Ca(OH)_2$.

Check Your Answer[6]

Due to their light sensitivity, mixtures of silver halides are used in fibre optics for medical lasers, in photochromic eyeglass lenses (glass lenses that automatically darken when exposed to sunlight), and—before the advent of digital photography—in photographic film. Even though AgCl ($K_{sp} = 1.6 \times 10^{-10}$), AgBr ($K_{sp} = 5.0 \times 10^{-13}$), and AgI ($K_{sp} = 1.5 \times 10^{-16}$) are each quite insoluble, we cannot prepare a homogeneous solid mixture of them by adding Ag^+ to a solution of Cl^-, Br^-, and I^-; essentially all of the AgI will precipitate before any of the other solid halides form because of its smaller value for K_{sp}. However, we can prepare a homogeneous mixture of the solids by slowly adding a solution of Cl^-, Br^-, and I^- to a solution of Ag^+.

When two anions form slightly soluble compounds with the same cation, or when two cations form slightly soluble compounds with the same anion, the less soluble compound (usually, the compound with the smaller K_{sp}) generally precipitates first when we add a precipitating agent to a solution containing both anions (or both cations). When the K_{sp} values of the two compounds differ by two orders of magnitude or more (e.g., 10^{-2} vs. 10^{-4}), almost all of the less soluble compound precipitates before any of the more soluble one does. This is an example of **selective precipitation**, where a reagent is added to a solution of dissolved ions causing one of the ions to precipitate out before the rest.

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (Figure 17.6d). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions (PO_4^{2-}) are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 17.6d Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: work by eutrophication&hypoxia, CC BY 2.0)

One common way to remove phosphates from water is by the addition of calcium hydroxide, known as lime, $Ca(OH)_2$. The lime is converted into calcium carbonate, a strong base, in the water. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3(OH)$, which then precipitates out of the solution:

$$5Ca^{2+} + 3PO_4{}^{3-} + OH^- \leftrightharpoons Ca_{10}(PO_4)_6 \cdot (OH)_2(s)$$

The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View Phosphorus Removal – Wastewater (https://science.jrank.org/pages/5146/Phosphorus-Removal.html) for more information on how phosphorus is removed from wastewater.

Common Ion Effect

As we saw when we discussed buffer solutions, the hydronium ion concentration of an aqueous solution of acetic acid decreases when the strong electrolyte sodium acetate, $NaCH_3CO_2$, is added. We can explain this effect using Le Châtelier's principle. The addition of acetate ions causes the equilibrium to shift to the left, decreasing the concentration of H_3O^+ to compensate for the increased acetate ion concentration. This increases the concentration of CH_3CO_2H:

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2{}^-$$

Because sodium acetate and acetic acid have the acetate ion in common, the influence on the equilibrium is called the **common ion effect**.

The common ion effect can also have a direct effect on solubility equilibria. Suppose we are looking at the reaction where silver iodide is dissolved:

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

If we were to add potassium iodide (KI) to this solution, we would be adding a substance that shares a common ion with silver iodide. Le Châtelier's principle tells us that when a change is made to a system at equilibrium, the reaction will shift to counteract that change. In this example, there would be an excess of iodide ions, so the reaction would shift toward the left, causing more silver iodide to precipitate out of solution.

Example 17.6i

Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide ($CdBr_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

The first thing you should notice is that the cadmium sulfide is dissolved in a solution that contains cadmium ions. We need to use an ICE table to set up this problem and include the $CdBr_2$ concentration as a contributor of cadmium ions:

$$\mathrm{CdS}(s) \leftrightharpoons \mathrm{Cd}^{2+}(aq) \ + \ \mathrm{S}^{2-}(aq)$$

	CdS $\rightleftharpoons$	Cd^{2+} +	S^{2-}
Initial concentration (*M*)		0.010	0
Change (*M*)		x	x
Equilibrium concentration (*M*)		$0.010 + x$	$0 + x = x$

$$K_{sp} = [\mathrm{Cd}^{2+}][\mathrm{S}^{2-}] = 1.0 \ \times \ 10^{-28}$$
$$(0.010 \ + \ x)(x) = 1.0 \ \times \ 10^{-28}$$
$$x^2 \ + \ 0.010x \ - \ 1.0 \ \times \ 10^{-28} \ = 0$$

We can solve this equation using the quadratic formula, but we can also make an assumption to make this calculation much simpler. Since the K_{sp} value is so small compared with the cadmium concentration, we can assume that the change between the initial concentration and the equilibrium concentration is negligible, so that $0.010 + x \sim 0.010$. Going back to our K_{sp} expression, we would now get:

$$K_{sp} = [\mathrm{Cd}^{2+}][\mathrm{S}^{2-}] = 1.0 \ \times \ 10^{-28}$$
$$(0.010)(x) = 1.0 \ \times \ 10^{-28}$$
$$x = 1.0 \ \times \ 10^{-26}$$

Therefore, the molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Exercise 17.6g

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015-*M* solution of aluminum nitrate, $Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Check Your Answer[7]

Key Equations

- $M_pX_q(s) \leftrightharpoons pM^{m+}(aq) + qX^{n-}(aq) \qquad K_{sp} = [M^{m+}]^p[X^{n-}]^q$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "15.1 Precipitation and Dissolution" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

1.
    a. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ba^{2+}][SO_4{}^{2-}]$;
    b. $Ag_2SO_4(s) \rightleftharpoons 2Ag^{+}(aq) + SO_4{}^{2-}(aq) \qquad K_{sp} = [Ag^{+}]^2[SO_4{}^{2-}]$;
    c. $Al(OH)_3(s) \rightleftharpoons Al^{2+}(aq) + 3OH^{-}(aq) \qquad K_{sp} = [Al^{3+}][OH^{-}]^3$;
    d. $Pb(OH)Cl(s) \rightleftharpoons Pb^{2+}(aq) + OH^{-}(aq) + Cl^{-}(aq) \qquad K_{sp} = [Pb^{2+}][OH^{-}][Cl^{-}]$
2. d) 8.99×10^{-12}
3. 1.2×10^{-8} *M*
4. No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$
5. 4.5×10^{-9} *M*
6. 10.97
7. 1×10^{-10} *M*

17.7 RELATIVE STRENGTHS OF ACIDS AND BASES

Learning Objectives

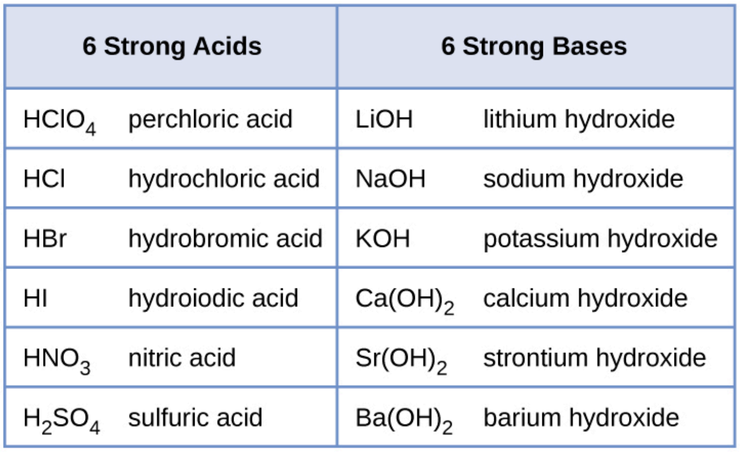
By the end of this section, you will be able to:

- 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, 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 H_3O^+ and A^- when the acid ionizes in water; Figure 17.7a lists several strong acids. A weak acid gives small amounts of H_3O^+ and A^-.



6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Figure 17.7a Some of the common strong acids and bases are listed here (credit: *Chemistry (OpenStax)*, CC BY 4.0).

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:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. 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.

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:

$$\%\ \mathrm{ionization} = \frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100$$

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 17.7a

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:

$$\frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HNO_2}]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$HNO_2(aq) \ + \ H_2O(l) \rightleftharpoons NO_2{}^-(aq) \ + \ H_3O^+(aq)$.

Since $10^{-pH} = [H_3O^+]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}$ *M*, so that percent ionization 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 17.7a

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89..

Check Your Answer[1]

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 17.7a 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.

Exercise 17.7b

Practice using the following PhET simulation: Acid and Base Solutions

(https://phet.colorado.edu/sims/html/acid-base-solutions/latest/acid-base-solutions_en.html)

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:

$$K_\mathrm{b} = \frac{[\mathrm{HB^+}][\mathrm{OH^-}]}{[\mathrm{B}]}$$

where the concentrations are those at equilibrium. Again, we do not include [H_2O] in the equation because water is the solvent. The chemical reactions and ionization constants of the three bases shown are:

$$\begin{aligned}
\mathrm{NO_2{}^-}(aq)\ +\ \mathrm{H_2O}(l)\ &\rightleftharpoons \mathrm{HNO_2}(aq)\ +\ \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 2.22\ \times\ 10^{-11}\\
\mathrm{CH_3CO_2{}^-}(aq)\ +\ \mathrm{H_2O}(l)\ &\rightleftharpoons \mathrm{CH_3CO_2H}(aq)\ +\ \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 5.6\ \times\ 10^{-10}\\
\mathrm{NH_3}(aq)\ +\ \mathrm{H_2O}(l)\ &\rightleftharpoons \mathrm{NH_4{}^+}(aq)\ +\ \mathrm{OH^-}(aq) \qquad K_\mathrm{b} = 1.8\ \times\ 10^{-5}
\end{aligned}$$

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, HA – A^-:

$$\mathrm{HA}(aq)\ +\ \mathrm{H_2O}(l)\ \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{A^-}(aq) \quad K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{A^-}(aq)\ +\ \mathrm{H_2O}(l)\ \rightleftharpoons \mathrm{OH^-}(aq)\ +\ \mathrm{HA}(aq) \quad K_\mathrm{b} = \frac{[\mathrm{HA}][\mathrm{OH}]}{[\mathrm{A^-}]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)}\ +\ \mathrm{H_2O}(l)\ +\ \cancel{\mathrm{A^-}(aq)}\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \cancel{\mathrm{A^-}(aq)}\ +\ \mathrm{OH^-}(aq)\ +\ \cancel{\mathrm{HA}(aq)}$$

$$\mathrm{2H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{OH^-}(aq)$$

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:

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

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 (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, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 17.7b).

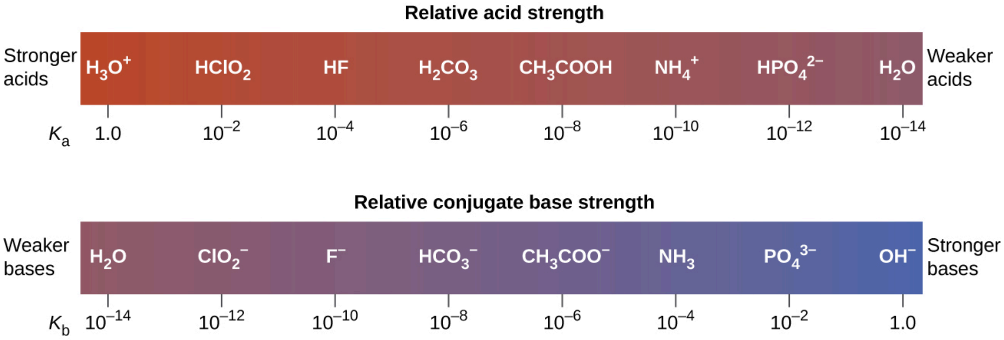
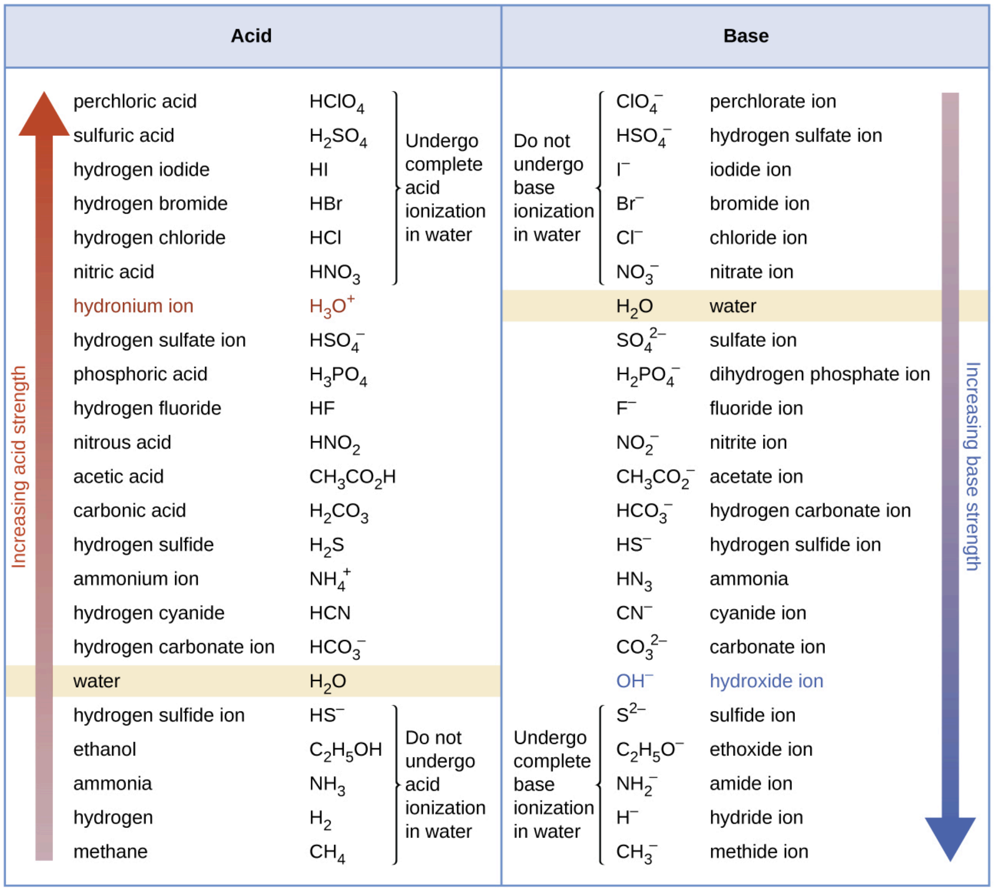


Figure 17.7b This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Figure 17.7c 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.



Acid				Base	
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			HN_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 17.7c The chart shows the relative strengths of conjugate acid-base pairs (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The first six acids in Figure 17.7c 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 17.7c 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 17.7c exhibit no observable acidic behaviour 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.

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 17.7c. A strong base, such as one of those lying below the 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 behaviour in aqueous solution.

Example 17.7b

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 Appendix I.

Exercise 17.7c

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 Appendix I 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^+.

Check Your Answer[2]

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:

$$\mathrm{CH_3CO_2H}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{CH_3CO_2{}^-}(aq),$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 17.7d). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{CH_3CO_2{}^-}]}{[\mathrm{CH_3CO_2H}]} = 1.8\ \times\ 10^{-5}$$

Figure 17.7d pH paper indicates that a 0.1-*M* solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 *M*. A 0.1-*M* solution of CH_3CO_2H (beaker on right) is 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 in *Chemistry (OpenStax)*, CC BY 4.0).

Table 17.7a 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}
$HCNO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	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}
$HCIO + H_2O \rightleftharpoons H_3O^+ + CIO^-$	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 17.7a gives the ionization constants for several weak acids; additional ionization constants can be found in Appendix I.

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:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq),$$

giving 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 17.7e). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the ionization constant of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$

Figure 17.7e 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, *Chemistry (OpenStax)*, CC BY 4.0).

The ionization constants of several weak bases are given in Table 17.7b and in Appendix J.

Table 17.7b 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 17.7c

Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 17.7f); that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-]$ = 0.00118M. What is the value of K_a for acetic acid?

Figure 17.7f Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by HomeSpot HQ, CC BY 2.0)

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:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2{}^-]}{[CH_3CO_2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Exercise 17.7d

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$\mathrm{HSO_4{}^-}(aq) \ + \ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) \ + \ \mathrm{SO_4{}^{2-}}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*, $[HSO_4^-]$ = 0.29 *M* and $[SO_4^{2-}]$ = 0.13 *M*.

Check Your Answer[3]

Example 17.7d

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:

$$\mathrm{C_8H_{10}N_4O_2}(aq) \ + \ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}N_4O_2H^+}(aq) \ + \ \mathrm{OH^-}(aq)$$

$$K_\mathrm{b} = \frac{[\mathrm{C_8H_{10}N_4O_2H^+}][\mathrm{OH^-}]}{[\mathrm{C_8H_{10}N_4O_2}]} = \frac{(5.0 \ \times \ 10^{-3})(2.5 \ \times \ 10^{-3})}{0.050} = 2.5 \ \times \ 10^{-4}$$

Exercise 17.7e

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, $[OH^-] = 1.3 \times 10^{-6}$ *M*, $[H_2PO_4{}^-] = 0.042$ *M* and $[HPO_4{}^{2-}] = 0.341$ *M*.

Check Your Answer[4]

Example 17.7e

Determination of K_a or K_b from pH

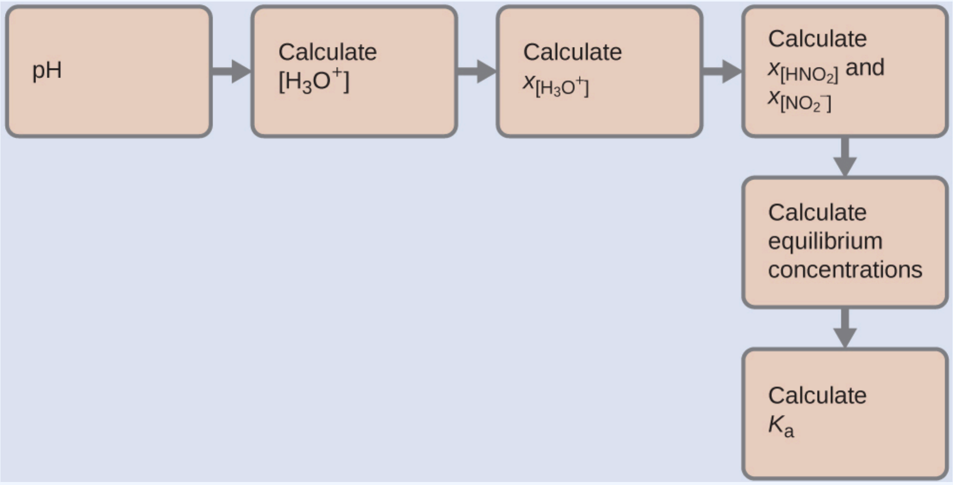
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq)$$

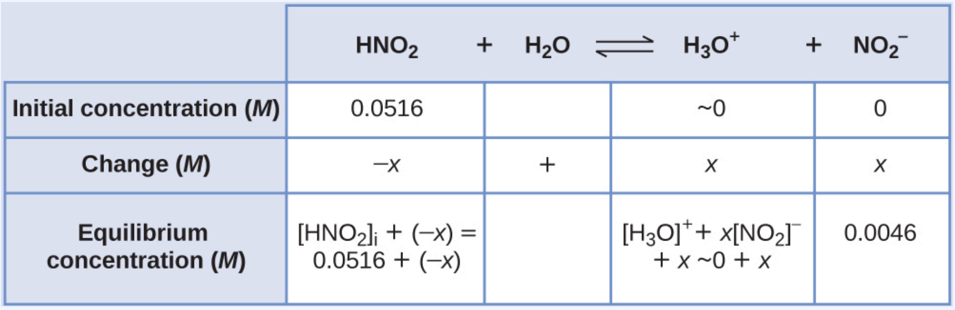
Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and $NO_2{}^-$ as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here (the concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its concentration):



	HNO_2	$+ \quad H_2O \rightleftharpoons$	H_3O^+	$+ \quad NO_2^-$
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

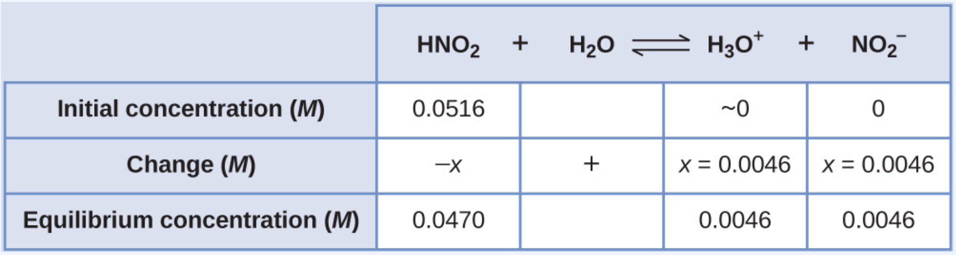
To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

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, $[H_3O^+]$. 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	$+ \quad H_2O \rightleftharpoons$	H_3O^+	$+ \quad NO_2^-$
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	$-x$	+	$x = 0.0046$	$x = 0.0046$
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2{}^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 17.7f

Check Your Learning Exercise (Text Version)
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?

a. 1.8×10^{-5}
b. 1.5×10^{-8}
c. 2.4×10^{-5}
d. 1.8×10^{-10}

Check Your Answer[5]

Source: "Exercise 17.7f" is adapted from "Example 14.3-5" in General Chemistry 1 & 2, a derivative of Chemistry (Open Stax) by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson, licensed under CC BY 4.0.

Example 17.7f

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 (Figure 17.7g).

Figure 17.7g The pain of an ant's sting is caused by formic acid. (credit: work by John Tann, CC BY 2.0)

What is the concentration of hydronium ion and the pH in a 0.534 *M* solution of formic acid?

$$\mathrm{HCO_2H}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{HCO_2}^-(aq)$$
$$K_\mathrm{a} = 1.8\ \times\ 10^{-4}$$

Solution

1. *Determine x and equilibrium concentrations*. The equilibrium expression is:
$$\mathrm{HCO_2H}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{HCO_2}^-(aq)$$
The concentration of water does not appear in the expression for the equilibrium constant, so we do not need to consider its change in concentration when setting up the ICE table.

   The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	HCO_2H +	H_2O $\rightleftharpoons$	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:

$$\begin{aligned} K_{\text{a}} &= 1.8 \times 10^{-4} \\ &= \frac{[\text{H}_3\text{O}^+][\text{HCO}_2{}^-]}{[\text{HCO}_2\text{H}]} \\ &= \frac{(x)(x)}{0.534 - x} \end{aligned}$$

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:

$$K_{\text{a}} = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$\begin{aligned} x^2 &= 0.534 \times (1.8 \times 10^{-4}) \\ &= 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} \end{aligned}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} \times (100) = \frac{9.8 \times 10^{-3}}{0.534} \times (100) = 1.8\% \leq 5\%$$

since x is less than 5% of the initial concentration (0.534 M), 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:

$$\begin{gathered} [\text{H}_3\text{O}^+] = {\sim}0 + x = 0 + 9.8 \times 10^{-3}\ M. \\ = 9.8 \times 10^{-3}\ M \end{gathered}$$

The pH of the solution can be found by taking the negative log of the $[\text{H}_3\text{O}^+]$, so:

$$-\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 17.7g

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?

$$\mathrm{CH_3CO_2H}(aq)\;+\;\mathrm{H_2O}(l)\rightleftharpoons\mathrm{H_3O^+}(aq)\;+\;\mathrm{CH_3CO_2{}^-}(aq)$$

$$K_\mathrm{a}=1.8\;\times\;10^{-5}$$

(Hint: Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or

$$\frac{[\mathrm{CH_3CO_2{}^-}]}{[\mathrm{CH_3CO_2H}]_\mathrm{initial}}\;\times\;100$$

Check Your Answer[6]

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 17.7g

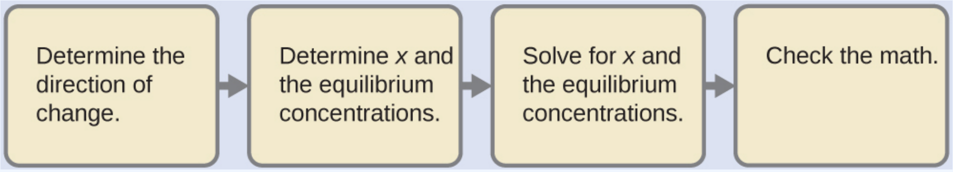
Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25 *M* solution of trimethylamine, a weak base:

$$\mathrm{(CH_3)_3N}(aq)\;+\;\mathrm{H_2O}(l)\rightleftharpoons\mathrm{(CH_3)_3NH^+}(aq)\;+\;\mathrm{OH^-}(aq)$$
$$K_\mathrm{b}=6.3\;\times\;10^{-5}$$

Solution

This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 17.7f. 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:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

If we assume that x is small relative to 0.25, then we can replace $(0.25 - x)$ in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$\begin{aligned}[OH^-] &= \sim 0 + x \\ &= x \\ &= 4.0 \times 10^{-3}\ M\end{aligned}$$

Then calculate pOH as follows:

$$\text{pOH} = -\log(4.0 \times 10^{-3}) = 2.40$$

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:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

3. *Check the work*. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

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 17.7h

Equilibrium Concentrations in a Solution of a Weak Acid

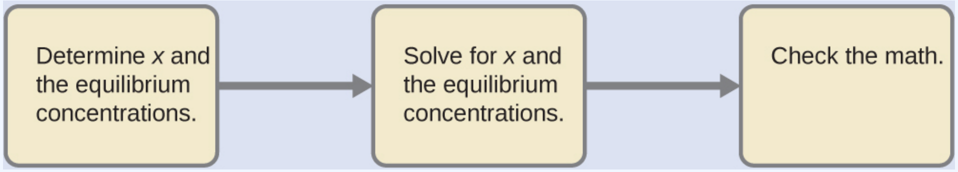
Sodium bisulfate, $NaHSO_4$, is used in some household cleansers because it contains the HSO_4^- ion, a weak acid. What is the pH of a 0.50-*M* solution of HSO_4^-?

$$\mathrm{HSO_4{}^-}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)\ +\ \mathrm{SO_4{}^{2-}}(aq)$$

$$K_\mathrm{a} = 1.2\ \times\ 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of HSO_4^- so that we can use $[H_3O^+]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. *Determine x and equilibrium concentrations*. This table shows the changes and concentrations:

	HSO_4^-	+ H_2O ⇌	H_3O^+	+ SO_4^{2-}
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.50 + (-x) =$ $0.50 - x)$		$0 + x = x$	$0 + x = x$

2. *Solve for x and the concentrations*. As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

   At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 – *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we calculate:

$$\frac{x}{[HSO_4{}^-]_i} \times (100) = \frac{7.7 \times 10^{-2}}{0.50} \times (100) = 15\%$$

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 equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this problem, *a* = 1, *b* = 1.2 × 10^{-3}, and *c* = −6.0 × 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:

$$[H_3O^+] = {\sim}0 + x = 0 + 7.2 \times 10^{-2}\ M$$

$$= 7.2 \times 10^{-2}\ M$$

The pH of this solution is:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log 7.2 \times 10^{-2} = 1.14$$

Exercise 17.7h

Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{H}^+(aq) + \text{OH}^-(aq)$$
$$K_\text{b} = 2.5 \times 10^{-4}$$

(Hint: It will be necessary to convert $[\text{OH}^-]$ to $[\text{H}_3\text{O}^+]$ or pOH to pH toward the end of the calculation.)

Check Your Answer[7]

Key Equations

- $K_\text{a} = \dfrac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
- $K_\text{b} = \dfrac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$
- $K_\text{a} \times K_\text{b} = 1.0 \times 10^{-14} = K_\text{w}$
- $\text{Percent ionization} = \dfrac{[\text{H}_3\text{O}^+]_\text{eq}}{[\text{HA}]_0} \times 100$

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "14.3 Strengths of Acids and Bases (https://boisestate.pressbooks.pub/chemistry/chapter/14-3-relative-strengths-of-acids-and-bases/)" In

General Chemistry 1 & 2 by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

1. 1.3% ionized
2. NH_4^+ is the slightly stronger acid (K_a for $NH_4^+ = 5.6 \times 10^{-10}$)
3. K_a for $HSO_4^- = 1.2 \text{ x } 10^{-2}$
4. K_b for $HPO_4^{2-} = 1.6 \text{ x } 10^{-7}$
5. a) $1.8 \text{ x } 10^{-5}$
6. percent ionization = 1.3%
7. pH 11.16

17.8 REAL WORLD EXAMPLES OF EQUILIBRIA

Learning Objectives

By the end of this section, you will be able to:

- Describe examples of systems involving two (or more) simultaneous chemical equilibria
- Calculate reactant and product concentrations for multiple equilibrium systems
- Compare dissolution and weak electrolyte formation

There are times when one equilibrium reaction does not adequately describe the system being studied. Sometimes we have more than one type of equilibrium occurring at once (for example, an acid-base reaction and a precipitation reaction).

The ocean is a unique example of a system with **multiple equilibria**, or multiple states of solubility equilibria working simultaneously. Carbon dioxide in the air dissolves in sea water, forming carbonic acid (H_2CO_3). The carbonic acid then ionizes to form hydrogen ions and bicarbonate ions (HCO_3^-), which can further ionize into more hydrogen ions and carbonate ions (CO_3^{2-}):

$$\begin{aligned} \mathrm{CO_2}(g) &\rightleftharpoons \mathrm{CO_2}(aq) \\ \mathrm{CO_2}(aq) + \mathrm{H_2O}(l) &\rightleftharpoons \mathrm{H_2CO_3}(aq) \\ \mathrm{H_2CO_3}(aq) &\rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HCO_3}^-(aq) \\ \mathrm{HCO_3}^-(aq) &\rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CO_3}^{2-}(aq) \end{aligned}$$

The excess H^+ ions make seawater more acidic. Increased ocean acidification can then have negative impacts on reef-building coral, as they cannot absorb the calcium carbonate they need to grow and maintain their skeletons (Figure 17.7a). This in turn disrupts the local biosystem that depends upon the health of the reefs for its survival. If enough local reefs are similarly affected, the disruptions to sea life can be felt globally. The world's oceans are presently in the midst of a period of intense acidification, believed to have begun in the mid-nineteenth century, and which is now accelerating at a rate faster than any change to oceanic pH in the last 20 million years.

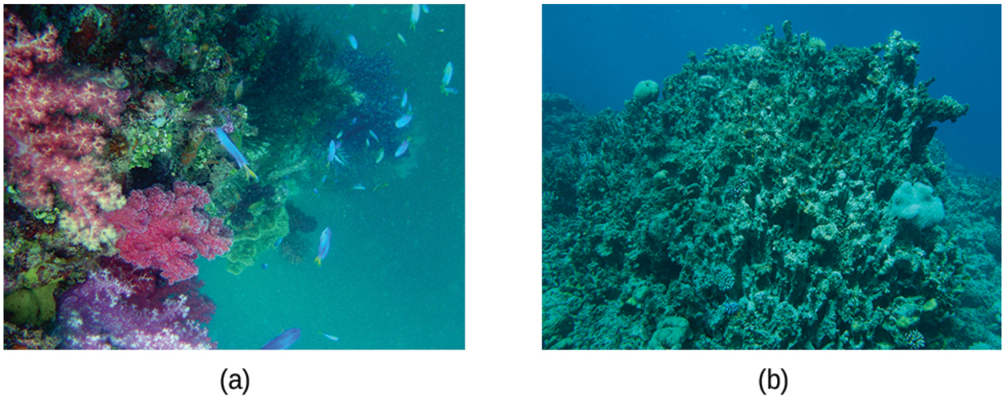


Figure 17.8a Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonite skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library, CC BY 2.0; credit b: modification of work by prilfish, CC BY 2.0)

Watch Can Corals Cope with Ocean Acidification? (3:36 min)

Slightly soluble solids derived from weak acids generally dissolve in strong acids, unless their solubility products are extremely small. For example, we can dissolve $CuCO_3$, FeS, and $Ca_3(PO_4)_2$ in HCl because their basic anions react to form weak acids (H_2CO_3, H_2S, and $H_2PO_4^-$). The resulting decrease in the concentration of the anion results in a shift of the equilibrium concentrations to the right in accordance with Le Châtelier’s principle.

Of particular relevance to us is the dissolution of hydroxylapatite, $Ca_5(PO_4)_3OH$, in acid. Apatites are a class of calcium phosphate minerals (Figure 17.7b); a biological form of hydroxylapatite is found as the principal mineral in the enamel of our teeth. A mixture of hydroxylapatite and water (or saliva) contains an equilibrium mixture of solid $Ca_5(PO_4)_3OH$ and dissolved Ca^{2+}, PO_4^{3-}, and OH^- ions:

$$\mathrm{Ca_5(PO_4)_3OH}(s) \longrightarrow 5\mathrm{Ca}^{2+}(aq) + 3\mathrm{PO_4}^{3-}(aq) + \mathrm{OH}^-(aq)$$

Figure 17.8b Crystal of the mineral hydroxylapatite, $Ca_5(PO_4)_3OH$, is shown here. Pure apatite is white, but like many other minerals, this sample is coloured because of the presence of impurities (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When exposed to acid, phosphate ions react with hydronium ions to form hydrogen phosphate ions and ultimately, phosphoric acid:

$$\mathrm{PO_4}^{3-}(aq) + \mathrm{H_3O^+} \rightleftharpoons \mathrm{H_2PO_4}^{2-} + \mathrm{H_2O}$$

$$\mathrm{PO_4}^{2-}(aq) + \mathrm{H_3O^+} \rightleftharpoons \mathrm{H_2PO_4}^{-} + \mathrm{H_2O}$$

$$\mathrm{H_2PO_4}^{-} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{H_3PO_4} + \mathrm{H_2O}$$

Hydroxide ion reacts to form water:

$$\mathrm{OH^-}(aq) + \mathrm{H_3O^+} \longrightarrow \mathrm{2H_2O}$$

These reactions decrease the phosphate and hydroxide ion concentrations, and additional hydroxylapatite dissolves in an acidic solution in accord with Le Châtelier's principle. Our teeth develop cavities when acid waste produced by bacteria growing on them causes the hydroxylapatite of the enamel to dissolve. Fluoride toothpastes contain sodium fluoride, NaF, or stannous fluoride [more properly named tin(II) fluoride], SnF_2. They function by replacing the OH^- ion in hydroxylapatite with F^- ion, producing fluorapatite, $Ca_5(PO_4)_3F$:

$$\mathrm{NaF} + \mathrm{Ca_5(PO_4)_3OH} \rightleftharpoons \mathrm{Ca_5(PO_4)_3F} + \mathrm{Na^+} + \mathrm{OH^-}$$

The resulting $Ca_5(PO_4)_3F$ is slightly less soluble than $Ca_5(PO_4)_3OH$, and F^- is a weaker base than OH^-. Both of these factors make the fluorapatite more resistant to attack by acids than hydroxylapatite. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $Ca_5(PO_4)_3F$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (Figure 17.7c).

Figure 17.8c Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk in *Chemistry (OpenStax)*, CC BY 4.0).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

When acid rain attacks limestone or marble, which are calcium carbonates, a reaction occurs that is similar to the acid attack on hydroxylapatite. The hydronium ion from the acid rain combines with the carbonate ion from calcium carbonates and forms the hydrogen carbonate ion, a weak acid:

$$H_3O^+(aq) + {CO_3}^{2-}(aq) \longrightarrow {HCO_3}^-(aq) + H_2O(l)$$

Calcium hydrogen carbonate, $Ca(HCO_3)_2$, is soluble, so limestone and marble objects slowly dissolve in acid rain.

If we add calcium carbonate to a concentrated acid, hydronium ion reacts with the carbonate ion according to the equation:

$$2H_3O^+(aq) \; + \; {CO_3}^{2-}(aq) \longrightarrow H_2CO_3(aq) \; + \; 2H_2O(l)$$

(Acid rain is usually not sufficiently acidic to cause this reaction; however, laboratory acids are.) The solution may become saturated with the weak electrolyte carbonic acid, which is unstable, and carbon dioxide gas can be evolved:

$$H_2CO_3(aq) \longrightarrow CO_2(g) \; + \; H_2O(l)$$

These reactions decrease the carbonate ion concentration, and additional calcium carbonate dissolves. If enough acid is present, the concentration of carbonate ion is reduced to such a low level that the reaction quotient for the dissolution of calcium carbonate remains less than the solubility product of calcium carbonate, even after all of the calcium carbonate has dissolved.

Example 17.8a

Prevention of Precipitation of $Mg(OH)_2$

Calculate the concentration of ammonium ion that is required to prevent the precipitation of $Mg(OH)_2$ in a solution with $[Mg^{2+}] = 0.10\ M$ and $[NH_3] = 0.10\ M$.

Solution

Two equilibria are involved in this system:

Reaction (1): $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) \; + \; 2OH^-(aq); \qquad K_{sp} = 8.9 \times 10^{-12}$

Reaction (2): $NH_3(aq) \; + \; H_2O(l) \rightleftharpoons {NH_4}^+(aq) \; + \; OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$

To prevent the formation of solid $Mg(OH)_2$, we must adjust the concentration of OH^- so that the reaction quotient for Equation (1), $Q = [Mg^{2+}][OH^-]^2$, is less than K_{sp} for $Mg(OH)_2$. (To simplify the calculation, we determine the concentration of OH^- when $Q = K_{sp}$.) $[OH^-]$ can be reduced by the addition of NH_4^+, which shifts Reaction (2) to the left and reduces $[OH^-]$.

1. *We determine the $[OH^-]$ at which $Q = K_{sp}$ when $[Mg^{2+}] = 0.10\ M$:*

$$Q = [Mg^{2+}][OH^-]^2 = (0.10)[OH^-]^2 = 8.9 \times 10^{-12}$$
$$[OH^-] = 9.4 \times 10^{-6}\ M$$

Solid $Mg(OH)_2$ will not form in this solution when $[OH^-]$ is less than 1.2×10^{-5} *M*.

2. *We calculate the $[NH_4^+]$ needed to decrease $[OH^-]$ to 1.2×10^{-5} M when $[NH_3] = 0.10$.*

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = \frac{[NH_4^+](9.4 \times 10^{-6})}{0.10} = 1.8 \times 10^{-5}$$

$$[NH_4{}^+] = 0.19\ M$$

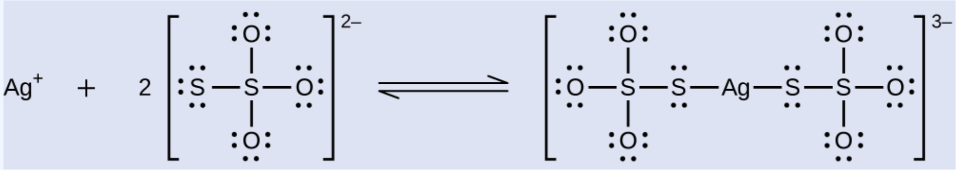
When $[NH_4^+]$ equals 0.19 *M*, $[OH^-]$ will be 9.4×10^{-6} *M*. Any $[NH_4^+]$ greater than 0.19 *M* will reduce $[OH^-]$ below 9.4×10^{-6} *M* and prevent the formation of $Mg(OH)_2$.

Therefore, precise calculations of the solubility of solids from the solubility product are limited to cases in which the only significant reaction occurring when the solid dissolves is the formation of its ions. For formation constants for complex ions, see Appendix L.

Example 17.8b

Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($Na_2S_2O_3$, called hypo) to form the complex ion $Ag(S_2O_3)_2{}^{3-}$ ($K_f = 4.7 \times 10^{13}$). The reaction with silver bromide is:



What mass of $Na_2S_2O_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $Ag(S_2O_3)_2{}^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $S_2O_3{}^{2-}$ ion:

Reaction (1): $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$

Reaction (2): $Ag^+(aq) + S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) \qquad K_f = 4.7 \times 10^{13}$

In order for 1.00 g of AgBr to dissolve, the $[Ag^+]$ in the solution that results must be low enough for *Q* for Reaction (1) to be smaller than K_{sp} for this reaction. We reduce $[Ag^+]$ by adding $S_2O_3^{2-}$ and thus cause Reaction (2) to shift to the right. We need the following steps to determine what mass of $Na_2S_2O_3$ is needed to provide the necessary $S_2O_3^{2-}$.

1. *We calculate the $[Br^-]$ produced by the complete dissolution of 1.00 g of AgBr (5.33×10^{-3} mol AgBr) in 1.00 L of solution:*
$$[\mathrm{Br}^-] = 5.33 \times 10^{-3}\ M$$
2. *We use $[Br^-]$ and K_{sp} to determine the maximum possible concentration of Ag^+ that can be present without causing reprecipitation of AgBr:*
$$[\mathrm{Ag}^+] = 9.4 \times 10^{-11}\ M$$
3. *We determine the* $[S_2O_3^{2-}]$ *required to make $[Ag^+] = 9.4 \times 10^{-11}$ M after the remaining Ag^+ ion has reacted with $S_2O_3^{2-}$ according to the equation:*
$$\mathrm{Ag}^+ + 2\mathrm{S_2O_3}^{2-} \rightleftharpoons \mathrm{Ag(S_2O_3)_2}^{3-} \qquad K_\mathrm{f} = 4.7 \times 10^{13}$$
Because 5.33×10^{-3} mol of AgBr dissolves:
$$(5.33 \times 10^{-3}) - (9.4 \times 10^{-11}) = 5.33 \times 10^{-3}\ \mathrm{mol\backslash Ag(S_2O_3)_2}^{3-}$$
Thus, at equilibrium: $[Ag(S_2O3)_2^{3-}] = 5.33 \times 10^{-3} M$, $[Ag^+] = 9.4 \times 10^{-11} M$, and $Q = K_f = 4.7 \times 10^{13}$:
$$K_\mathrm{f} = \frac{[\mathrm{Ag(S_2O_3)_2}^{3-}]}{[\mathrm{Ag}^+][\mathrm{S_2O_3}^{2-}]^2} = 4.7 \times 10^{13}$$
$$[\mathrm{S_2O_3}^{2-}] = 1.1 \times 10^{-3}\ M$$
When $[S_2O_3^{2-}]$ is $1.1 \times 10^{-3} M$, $[Ag^+]$ is $9.4 \times 10^{-11} M$ and all AgBr remains dissolved.
4. *We determine the total number of moles of* $S_2O_3^{2-}$ *that must be added to the solution.* This equals the amount that reacts with Ag^+ to form $Ag(S_2O3)_2^{3-}$ plus the amount of free $S_2O_3^{2-}$ in solution at equilibrium. To form 5.33×10^{-3} mol of $Ag(S_2O3)_2^{3-}$ requires $2 \times (5.33 \times 10^{-3})$ mol of $S_2O_3^{2-}$. In addition, 1.1×10^{-3} mol of unreacted $S_2O_3^{2-}$ is present (Step 3). Thus, the total amount of $S_2O_3^{2-}$ that must be added is:
$$2 \times (5.33 \times 10^{-3}\ \mathrm{mol\backslash S_2O_3}^{2-}) + 1.1 \times 10^{-3}\ \mathrm{mol\backslash S_2O_3}^{2-} = 1.18 \times 10^{-2}\ \mathrm{mol\backslash S_2O_3}^{2-}$$
5. *We determine the mass of $Na_2S_2O_3$ required to give 1.18×10^{-2} mol* $S_2O_3^{2-}$ *using the molar mass of $Na_2S_2O_3$:*
$$1.18 \times 10^{-2}\ \mathrm{mol\backslash S_2O_3}^{2-} \times \frac{158.1\ \mathrm{g\backslash Na_2S_2O_3}}{1\ \mathrm{mol\backslash Na_2S_2O_3}} = 1.9\ \mathrm{g\backslash Na_2S_2O_3}$$
Thus, 1.00 L of a solution prepared from 1.9 g $Na_2S_2O_3$ dissolves 1.0 g of AgBr.

Exercise 17.8a

AgCl(*s*), silver chloride, is well known to have a very low solubility: $\mathrm{Ag}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$, $K_{sp} = 1.6 \times 10^{-10}$. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $\mathrm{Ag}^{+}(aq) + 2\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2}^{+}(aq)$, $K_f = 1.7 \times 10^{7}$. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $Ag(NH_3)_2^{+}$?

Check Your Answer[1]

Dissolution versus Weak Electrolyte Formation

We can determine how to shift the concentration of ions in the equilibrium between a slightly soluble solid and a solution of its ions by applying Le Châtelier's principle. For example, one way to control the concentration of manganese(II) ion, Mn^{2+}, in a solution is to adjust the pH of the solution and, consequently, to manipulate the equilibrium between the slightly soluble solid manganese(II) hydroxide, manganese(II) ion, and hydroxide ion:

$$\mathrm{Mn(OH)_2}(s) \rightleftharpoons \mathrm{Mn}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) \qquad K_{sp} = [\mathrm{Mn}^{2+}][\mathrm{OH}^{-}]^2$$

This could be important to a laundry because clothing washed in water that has a manganese concentration exceeding 0.1 mg per litre may be stained by the manganese. We can reduce the concentration of manganese by increasing the concentration of hydroxide ion. We could add, for example, a small amount of NaOH or some other base such as the silicates found in many laundry detergents. As the concentration of OH^{-} ion increases, the equilibrium responds by shifting to the left and reducing the concentration of Mn^{2+} ion while increasing the amount of solid $Mn(OH)_2$ in the equilibrium mixture, as predicted by Le Châtelier's principle.

Example 17.8c

Solubility Equilibrium of a Slightly Soluble Solid

What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ in water at equilibrium?

a. $MgCl_2$
b. KOH
c. an acid
d. $NaNO_3$
e. $Mg(OH)_2$

Solution

The equilibrium among solid $Mg(OH)_2$ and a solution of Mg^{2+} and OH^- is:

$$\mathbf{Mg(OH)_2}(s) \rightleftharpoons \mathbf{Mg^{2+}}(aq) + \mathbf{2OH^-}(aq)$$

a. The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Châtelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{sp}$), and $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.
b. The reaction shifts to the left to relieve the stress of the additional OH^- ion. $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is greater and $[Mg^{2+}]$ is less than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.
c. The concentration of OH^- is reduced as the OH^- reacts with the acid. The reaction shifts to the right to relieve the stress of less OH^- ion. In quantitative terms, the decrease in the OH^- concentration causes the reaction quotient to be smaller than the solubility product ($Q < K_{sp}$), and additional $Mg(OH)_2$ dissolves until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More $Mg(OH)_2$ is dissolved.
d. $NaNO_3$ contains none of the species involved in the equilibrium, so we should expect that it has no appreciable effect on the concentrations of Mg^{2+} and OH^-. (As we have seen previously, dissolved salts change the activities of the ions of an electrolyte. However, the salt effect is generally small, and we shall neglect the slight errors that may result from it.)
e. The addition of solid $Mg(OH)_2$ has no effect on the solubility of $Mg(OH)_2$ or on the concentration

of Mg^{2+} and OH^-. The concentration of $Mg(OH)_2$ does not appear in the equation for the reaction quotient:

$$Q = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of *Q*, and no shift is required to restore *Q* to the value of the equilibrium constant.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "15.3 Coupled Equilibria (https://boisestate.pressbooks.pub/chemistry/chapter/15-3-coupled-equilibria/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)*

Notes

1. 1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

CHAPTER 17 - SUMMARY

17.1 Chemical Reaction Rates

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

17.2 Chemical Equilibria

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

17.3 Equilibrium Constants

For any reaction that is at equilibrium, the reaction quotient Q is equal to the equilibrium constant K for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal K (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

17.4 Shifting Equilibria: Le Châtelier's Principle

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 Châtelier'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.

17.5 Equilibrium Calculations

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of X is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium.

17.6 Precipitation and Dissolution

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp}, of the solid. When we have a heterogeneous equilibrium involving the slightly soluble solid M_pX_q and its ions $\text{M}^{\text{m+}}$ and $\text{X}^{\text{n-}}$:

$$\text{M}_p\text{X}_q(s) \leftrightharpoons p\text{M}^{\text{m+}}(aq) \;+\; q\text{X}^{\text{n-}}(aq)$$

We write the solubility product expression as:

$$K_{\text{sp}} = [\text{M}^{\text{m+}}]^p[\text{X}^{\text{n-}}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp}, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions.

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.

A reagent can be added to a solution of ions to allow one ion to selectively precipitate out of solution. The common ion effect can also play a role in precipitation reactions. In the presence of an ion in common with one of the ions in the solution, Le Châtelier's principle applies and more precipitate comes out of solution so that the molar solubility is reduced.

17.7 Relative Strengths of Acids and Bases

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 [$H_2SeO_4 < H_2SO_4$].

17.8 Real World Examples of Equilibria

Several systems we encounter consist of multiple equilibria, systems where two or more equilibria processes are occurring simultaneously. Some common examples include acid rain, fluoridation, and dissolution of carbon dioxide in sea water. When looking at these systems, we need to consider each equilibrium separately and then combine the individual equilibrium constants into one solubility product or reaction quotient expression using the tools from the first equilibrium chapter. Le Châtelier's principle also must be considered, as each reaction in a multiple equilibria system will shift toward reactants or products based on what is added to the initial reaction and how it affects each subsequent equilibrium reaction.

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "12.1 Chemical Reaction Rates", "13.1 Chemical Equilibria", "13.2 Equilibrium Constants", "13.3 Shifting Equilibria: Le Chatelier's Principle", "13.4 Equilibrium Calculations", "14.3 Strengths of Acids and Bases" (https://boisestate.pressbooks.pub/chemistry/chapter/14-3-relative-strengths-of-acids-and-bases/), "15.1 Precipitation and Dissolution" and "15.3 Coupled Equilibria (https://boisestate.pressbooks.pub/chemistry/chapter/15-3-coupled-equilibria/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)* . / End of page key takeaways/summaries extracted and reused.

CHAPTER 17 - REVIEW

17.1 Chemical Reaction Rates

1. What is the difference between average rate, initial rate, and instantaneous rate? **Check Answer:** [1]
2. Ozone decomposes to oxygen according to the equation $2O_3(g) \longrightarrow 3O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.
3. In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3. **Check Answer:** [2]
4. A study of the rate of dimerization of C_4H_6 gave the data shown in the table below: $2C_4H_6 \longrightarrow C_8H_{12}$

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

   a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
   b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?
   c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).
5. A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data as shown in the table below:

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

   a. Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
   b. Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*].

What are the units of this rate?

   c. Use the rates found in parts (a) and (b) to determine the average rate of formation of *B* between 0.00 s and 10.0 s, and the instantaneous rate of formation of *B* at 15.0 s.
   Check Answer: [3]

6. Consider the following reaction in aqueous solution:

$$5\text{Br}^-(aq) + \text{BrO}_3{}^-(aq) + 6\text{H}^+(aq) \longrightarrow 3\text{Br}_2(aq) + 3\text{H}_2\text{O}(l)$$

   If the rate of disappearance of $\text{Br}^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4} M\,s^{-1}$, what is the rate of appearance of $\text{Br}_2(aq)$ at that moment?

17.2 Chemical Equilibria

1. What does it mean to describe a reaction as "reversible"? **Check Answer:** [4]
2. When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?
3. If a reaction is reversible, when can it be said to have reached equilibrium? **Check Answer:** [5]
4. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?
5. If the concentrations of products and reactants are equal, is the system at equilibrium? **Check Answer:** [6]

17.3 Equilibrium Constants

1. Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.
2. Explain why an equilibrium between $\text{Br}_2(l)$ and $\text{Br}_2(g)$ would not be established if the container were not a closed vessel. **Check Answer:** [7]
3. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?
   $$2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$$
4. Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, PbCl_2, and CuCl.
   a. Write the expression for the equilibrium constant for the reaction represented by the equation $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
   b. Write the expression for the equilibrium constant for the reaction represented by the equation $\text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq) \rightleftharpoons \text{PbCl}_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
   Check Answer: [8]
5. Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and

arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

a. Write the expression for the equilibrium constant for the reaction represented by the equation $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

b. Write the expression for the equilibrium constant for the reaction represented by the equation $3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

6. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer. **Check Answer:** [9]
7. Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and $I_3{}^-$.
8. For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction? **Check Answer:** [10]
9. For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?
10. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:
    a. $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$
    b. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
    c. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
    d. $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$
    e. $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$
    f. $Br_2(g) \rightleftharpoons 2Br(g)$
    g. $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$
    h. $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

    Check Answer: [11]
11. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:
    a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
    b. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
    c. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
    d. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
    e. $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
    f. $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$
    g. $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$
    h. $S_8(g) \rightleftharpoons 8S(g)$

12. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.
    a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad K_c = 17$; $[NH_3] = 0.20\ M$, $[N_2] = 1.00\ M$, $[H_2] = 1.00\ M$
    b. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 3.0 atm, N_2 = 2.0 atm, H_2 = 1.0 atm
    c. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$; $[SO_3] = 0.00\ M$, $[SO_2] = 1.00\ M$, $[O_2] = 1.00\ M$
    d. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_P = 16.5$; initial pressures: SO_3 = 1.00 atm, SO_2 = 1.00 atm, O_2 = 1.00 atm
    e. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 4.6 \times 10^4$; $[NO] = 1.00\ M$, $[Cl_2] = 1.00\ M$, $[NOCl] = 0\ M$
    f. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_P = 0.050$; initial pressures: NO = 10.0 atm, N_2 = O_2 = 5 atm

    Check Answer: [12]
13. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.
    a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad K_c = 17$; $[NH_3] = 0.50\ M$, $[N_2] = 0.15\ M$, $[H_2] = 0.12\ M$
    b. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm
    c. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$; $[SO_3] = 2.00\ M$, $[SO_2] = 2.00\ M$, $[O_2] = 2.00\ M$
    d. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_P = 6.5\ \text{atm}$; initial pressures: SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm
    e. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_P = 2.5 \times 10^3$; initial pressures: NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm
    f. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = 0.050$; $[N_2] = 0.100\ M$, $[O_2] = 0.200\ M$, $[NO] = 1.00\ M$
14. The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

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

    If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52 **Check Answer:** [13]
15. Determine if the following system is at equilibrium. If not, in which direction will the system need to

shift to reach equilibrium?

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

$[SO_2Cl_2] = 0.12\ M$, $[Cl_2] = 0.16\ M$ and $[SO_2] = 0.050\ M$. K_c for the reaction is 0.078.

16. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.
    a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ ^\circ C$
    b. $H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$
    c. $Na_2SO_4{\cdot}10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ ^\circ C$
    d. $H_2O(l) \rightleftharpoons H_2O(g) \qquad K_P = 0.122 \text{ at } 50\ ^\circ C$

    Check Answer: [14]
17. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.
    a. $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_c = 4.7 \times 10^{-2} \text{ at } 25\ ^\circ C$
    b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_P = 48.2 \text{ at } 500\ ^\circ C$
    c. $CaCl_2{\cdot}6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$
    d. $H_2O(l) \rightleftharpoons H_2O(g) \qquad K_P = 0.196 \text{ at } 60\ ^\circ C$
18. What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$ at 30 °C? **Check Answer:** [15]
19. Write the expression of the reaction quotient for the ionization of HOCN in water.
20. Write the reaction quotient expression for the ionization of NH_3 in water.**Check Answer:** [16]
21. What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (Vapour pressure was described in the previous chapter on liquids and solids; refer back to this chapter to find the relevant information needed to solve this problem.)

17.4 Shifting Equilibria: Le Châtelier's Principle

1. The following equation represents a reversible decomposition:

   $$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

   Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains? **Check Answer:** [17]
2. Explain how to recognize the conditions under which changes in pressure would affect systems at equilibrium.
3. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant? **Check Answer:** [18]
4. What would happen to the colour of the solution in part (b) of Figure 17.4a if a small amount of NaOH were added and $Fe(OH)_3$ precipitated? Explain your answer.
5. The following reaction occurs when a burner on a gas stove is lit:

$CH_4(g)\ +\ 2O_2(g) \rightleftharpoons CO_2(g)\ +\ 2H_2O(g)$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer. **Check Answer:** [19]

6. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

   $2SO_2(g)\ +\ O_2(g) \longrightarrow 2SO_3(g)$

   a. Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
   b. Is the reaction endothermic or exothermic?

7. Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

   $P_4(g)\ +\ 6H_2(g) \rightleftharpoons 4PH_3(g) \qquad \Delta H = 110.5\ \text{kJ}$

   Check Answer: [20]

8. Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:

   $H_2O(g)\ +\ C(s) \rightleftharpoons H_2(g)\ +\ CO(g)$. Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

   a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

      $2H_2(g)\ +\ CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.2\ \text{kJ}$
   b. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
   c. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?
   d. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?
   e. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?
   f. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

9. Nitrogen and oxygen react at high temperatures.

   a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

      $N_2(g)\ +\ O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181\ \text{kJ}$
   b. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?
   c. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

   d. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?
   e. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
   f. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?
   g. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?
   Check Answer:
10. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.
   a. Write the expression for the equilibrium constant for the reversible reaction
   $$\mathrm{C}(s) \ + \ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) \ + \ \mathrm{H_2}(g) \qquad \Delta H = 131.30 \text{ kJ}$$
   b. What will happen to the concentration of each reactant and product at equilibrium if more C is added?
   c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
   d. What will happen to the concentration of each reactant and product at equilibrium if CO is added?
   e. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?
11. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.
   a. Write the expression for the equilibrium constant (K_c) for the reversible reaction
   $$\mathrm{Fe_2O_3}(s) \ + \ 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{Fe}(s) \ + \ 3\mathrm{H_2O}(g) \qquad \Delta H = 98.7 \text{ kJ}$$
   b. What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?
   c. What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?
   d. What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?
   e. What will happen to the concentration of each reactant and product at equilibrium if the pressure on the system is increased by reducing the volume of the reaction vessel?
   f. What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?
   Check Answer: [21]
12. Ammonia is a weak base that reacts with water according to this equation:
   $$\mathrm{NH_3}(aq) \ + \ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4}^+(aq) \ + \ \mathrm{OH}^-(aq)$$
   Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?
   a. Addition of NaOH

   b. Addition of HCl
   c. Addition of NH_4Cl

13. Acetic acid is a weak acid that reacts with water according to this equation:

    $$CH_3CO_2H(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

    Will any of the following increase the percent of acetic acid that reacts and produces $CH_3CO_2{}^-$ ion?

    a. Addition of HCl
    b. Addition of NaOH
    c. Addition of $NaCH_3CO_2$

    Check Answer: [22]

14. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and $NO_3{}^-$, in contact with solid AgCl.

    $$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3{}^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3{}^-(aq)$$

    $$\Delta H = -65.9 \text{ kJ}$$

15. How can the pressure of water vapor be increased in the following equilibrium?

    $$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta H = 41 \text{ kJ}$$

    Check Answer: [23]

16. Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.

    $$2Ag^+(aq) + SO_4{}^{2-}(aq) \rightleftharpoons Ag_2SO_4(s)$$

    Which of the following will occur?

    a. Ag^+ or $SO_4{}^{2-}$ concentrations will not change.
    b. The added silver sulfate will dissolve.
    c. Additional silver sulfate will form and precipitate from solution as Ag^+ ions and $SO_4{}^{2-}$ ions combine.
    d. The Ag^+ ion concentration will increase and the $SO_4{}^{2-}$ ion concentration will decrease.

17. The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization $(HX \rightleftharpoons H^+ + X^-)$?

    Check Answer: [24]

17.5 Equilibrium Calculations

1. A reaction is represented by this equation: $A(aq) + 2B(aq) \rightleftharpoons 2C(aq) \qquad K_c = 1 \times 10^3$

   a. Write the mathematical expression for the equilibrium constant.
   b. Using concentrations ≤1 M, make up two sets of concentrations that describe a mixture of A, B,

and C at equilibrium.

Check Answer: [25]

2. A reaction is represented by this equation:

   $$2\text{W}(aq) \rightleftharpoons \text{X}(aq) + 2\text{Y}(aq) \qquad K_c = 5 \times 10^{-4}$$

   a. Write the mathematical expression for the equilibrium constant.
   b. Using concentrations of ≤1 *M*, make up two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.
3. What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

   $$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$$

   An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

   Check Answer: [26]
4. Hydrogen is prepared commercially by the reaction of methane and water vapour at elevated temperatures.

   $$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons 3\text{H}_2(g) + \text{CO}(g)$$

   What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?
5. A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature. **Check Answer:** [27]
6. At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 3.3×10^{-3}% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

   $$2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g)$$
7. Calculate the value of the equilibrium constant K_P for the reaction

   $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm. **Check Answer:** [28]
8. When heated, iodine vapor dissociates according to this equation:

   $$\text{I}_2(g) \rightleftharpoons 2\text{I}(g)$$

   At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.
9. A sample of ammonium chloride was heated in a closed container.

   $$\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)$$

   At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature? **Check Answer:** [29]
10. At a temperature of 60 °C, the vapour pressure of water is 0.196 atm. What is the value of the

equilibrium constant K_P for the transformation at 60 °C?

$$H_2O(l) \rightleftharpoons H_2O(g)$$

11. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions in the table below.

a.		$2\ SO_3\ (g)$	$\rightleftharpoons$	$2\ SO_2\ (g)$	$+\ O_2\ (g)$
		______		______	+x
		______		______	0.125 M
b.	$4\ NH_3\ (g)$	$+\ 3\ O_2\ (g)$	$\rightleftharpoons$	$2\ N_2\ (g)$	$+\ 6\ H_2O\ (g)$
	______	3x		______	______
	______	0.24 M		______	______
c.		$2\ CH_4\ (g)$	$\rightleftharpoons$	$C_2H_2\ (g)$	$+\ 3\ H_2\ (g)$
		______		x	______
		______		25 torr	______
d.	$CH_4\ (g)$	$+\ H_2O\ (g)$	$\rightleftharpoons$	$CO\ (g)$	$+\ 3\ H_2\ (g)$
	______	x		______	______
	______	5 atm		______	______
e.		$NH_4Cl\ (s)$	$\rightleftharpoons$	$NH_3\ (g)$	$+\ HCl\ (g)$
				x	______
				1.03×10^{-4} M	______
f.	$Ni\ (s)$	$+\ 4\ CO\ (g)$	$\rightleftharpoons$	$Ni(CO)_4\ (g)$	
		4x		______	
		0.40 atm		______	

Check Answer: [30]

12. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions in the table below.

a.	$2\ H_2\,(g)$	$+\ O_2\,(g)$	$\rightleftharpoons$	$2\ H_2O\,(g)$	
	______	______		+2x	
	______	______		1.50 M	
b.	$CS_2\,(g)$	$+\ 4\ H_2\,(g)$	$\rightleftharpoons$	$CH_4\,(g)$	$+\ 2\ H_2S\,(g)$
	x	______		______	______
	0.020 M	______		______	______
c.	$H_2\,(g)$	$+\ Cl_2\,(g)$	$\rightleftharpoons$	$2\ HCl\,(g)$	
	x	______		______	
	1.50 atm	______		______	
d.	$2\ NH_3\,(g)$	$+\ 2\ O_2\,(g)$	$\rightleftharpoons$	$N_2O\,(g)$	$+\ 3\ H_2O\,(g)$
	______	______		______	x
	______	______		______	60.6 torr
e.		$NH_4HS\,(s)$	$\rightleftharpoons$	$NH_3\,(g)$	$+\ H_2S\,(g)$
				x	______
				9.8×10^{-6} M	______
f.	$Fe\,(s)$	$+\ 5\ CO\,(g)$	$\rightleftharpoons$	$Fe(CO)_4\,(g)$	
		______		x	
		______		0.012 atm	

13. Why are there no changes specified for Ni in Exercise 11, part (f) above? What property of Ni does change? **Check Answer:** [31]
14. Why are there no changes specified for NH_4HS in Exercise 12, part (e) above? What property of NH_4HS does change?
15. Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 M and the concentration of H_2 to be 0.24 M.

$$N_2(g)\ +\ 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ ^\circ\text{C}$$

    Calculate the equilibrium molar concentration of NH_3. **Check Answer:** [32]
16. Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$H_2\ +\ I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ\text{C}$$

17. What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?
    $$\mathrm{Cl_2}(g)\ +\ \mathrm{Br_2}(g) \rightleftharpoons \mathrm{2BrCl}(g) \qquad K_P = 4.7\ \times\ 10^{-2}$$
    Check Answer: [33]
18. What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?
    $$\mathrm{H_2}(g)\ +\ \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g)\ +\ \mathrm{CO}(g) \qquad K_P = 1.6 \text{ at } 990\ ^\circ\mathrm{C}$$
19. Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.
    $$\mathrm{CoO}(s)\ +\ \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s)\ +\ \mathrm{CO_2}(g) \qquad K_c = 4.90\ \times\ 10^{2} \text{ at } 550\ ^\circ\mathrm{C}$$
    What concentration of CO remains in an equilibrium mixture with $[CO_2]$ = 0.100 *M*? **Check Answer:** [34]
20. Carbon reacts with water vapour at elevated temperatures.
    $$\mathrm{C}(s)\ +\ \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g)\ +\ \mathrm{H_2}(g) \qquad K_c = 0.2 \text{ at } 1000\ ^\circ\mathrm{C}$$
    What is the concentration of CO in an equilibrium mixture with $[H_2O]$ = 0.500 *M* at 1000 °C?
21. Sodium sulfate 10–hydrate, $Na_2SO_4{\cdot}10H_2O$, dehydrates according to the equation
    $$\mathrm{Na_2SO_4{\cdot}10H_2O}(s) \rightleftharpoons \mathrm{Na_2SO_4}(s)\ +\ \mathrm{10H_2O}(g) \qquad K_P = 4.08\ \times\ 10^{-25} \text{ at } 25\ ^\circ\mathrm{C}$$
    What is the pressure of water vapour at equilibrium with a mixture of $Na_2SO_4{\cdot}10H_2O$ and $NaSO_4$? **Check Answer:** [35]
22. Calcium chloride 6–hydrate, $CaCl_2{\cdot}6H_2O$, dehydrates according to the equation
    $$\mathrm{CaCl_2{\cdot}6H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s)\ +\ \mathrm{6H_2O}(g) \qquad K_P = 5.09\ \times\ 10^{-44} \text{ at } 25\ ^\circ\mathrm{C}$$
    What is the pressure of water vapour at equilibrium with a mixture of $CaCl_2{\cdot}6H_2O$ and $CaCl_2$?
23. A student solved the following problem and found the equilibrium concentrations to be $[SO_2]$ = 0.590 *M*, $[O_2]$ = 0.0450 *M*, and $[SO_3]$ = 0.260 *M*. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:
    $$\mathrm{2SO_2}(g)\ +\ \mathrm{O_2}(g) \rightleftharpoons \mathrm{2SO_3}(g) \qquad K_c = 4.32$$
    What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3]$ = 0.500 *M*, $[SO_2]$ = 0 *M*, and $[O_2]$ = 0.350 *M*? **Check Answer:** [36]
24. A student solved the following problem and found $[N_2O_4]$ = 0.16 *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?
    $$\mathrm{2NO_2}(g) \rightleftharpoons \mathrm{N_2O_4}(g) \qquad K_c = 160$$
25. Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.
    a. Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.
       $$\mathrm{N_2O_4}(g) \leftrightarrows \mathrm{2NO_2}(g) \qquad K_c = 1.07\ \times\ 10^{-5} \text{ in chloroform}$$

   b. Show that the change is small enough to be neglected.
      Check Answer: [37]
26. Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.
   a. Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.
      $$\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g) \qquad K_c = 2.2 \times 10^{-10}$$
   b. Show that the change is small enough to be neglected.
27. Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.
   a. Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.
      $$2\text{H}_2\text{S}(g) \rightleftharpoons 2\text{H}_2(g) + \text{S}_2(g) \qquad K_P = 2.2 \times 10^{-6}$$
   b. Show that the change is small enough to be neglected. **Check Answer:** [38]
28. What are all concentrations after a mixture that contains $[H_2O]$ = 1.00 *M* and $[Cl_2O]$ = 1.00 *M* comes to equilibrium at 25 °C?
   $$\text{H}_2\text{O}(g) + \text{Cl}_2\text{O}(g) \rightleftharpoons 2\text{HOCl}(g) \qquad K_c = 0.0900$$
29. What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5]$ = 2.00 *M*?
   $$\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \qquad K_c = 0.0211$$
   Check Answer: [39]
30. Calculate the pressures of all species at equilibrium in a mixture of NOCl, NO, and Cl_2 produced when a sample of NOCl with a pressure of 10.0 atm comes to equilibrium according to this reaction:
   $$2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g) \qquad K_P = 4.0 \times 10^{-4}$$
31. Calculate the equilibrium concentrations of NO, O_2, and NO_2 in a mixture at 250 °C that results from the reaction of 0.20 *M* NO and 0.10 *M* O_2. (Hint: *K* is large; assume the reaction goes to completion then comes back to equilibrium.) **Check Answer:** [40]
   $$2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \qquad K_c = 2.3 \times 10^5 \text{ at } 250\ ^\circ\text{C}$$
32. Calculate the equilibrium concentrations that result when 0.25 *M* O_2 and 1.0 *M* HCl react and come to equilibrium.
   $$4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g) \qquad K_c = 3.1 \times 10^{13}$$
33. One of the important reactions in the formation of smog is represented by the equation
   $$\text{O}_3(g) + \text{NO}(g) \rightleftharpoons \text{NO}_2(g) + \text{O}_2(g) \qquad K_P = 6.0 \times 10^{34}$$
   What is the pressure of O_3 remaining after a mixture of O_3 with a pressure of 1.2×10^{-8} atm and NO with a pressure of 1.2×10^{-8} atm comes to equilibrium? (Hint: K_P is large; assume the reaction goes to completion then comes back to equilibrium.) **Check Answer:** [41]
34. Calculate the pressures of NO, Cl_2, and NOCl in an equilibrium mixture produced by the reaction of a starting mixture with 4.0 atm NO and 2.0 atm Cl_2. (Hint: K_P is small; assume the reverse reaction goes

to completion then comes back to equilibrium.)

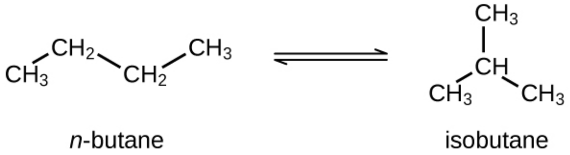
$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_P = 2.5 \times 10^3$$

35. Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ C$$

Check Answer: [42]

36. Butane exists as two isomers, *n*–butane and isobutane shown in the figure below with K_P = 2.5 at 25 °C.



What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

37. What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.050 for the decomposition reaction of $CaCO_3$ at that temperature?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Check Answer: [43]

38. The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

39. At 25 °C and at 1 atm, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are $P_{N_2O_4} = 0.70 \text{ atm}$ and $P_{NO_2} = 0.30 \text{ atm}$.
    a. Predict how the pressures of NO_2 and N_2O_4 will change if the total pressure increases to 9.0 atm. Will they increase, decrease, or remain the same?
    b. Calculate the partial pressures of NO_2 and N_2O_4 when they are at equilibrium at 9.0 atm and 25 °C. **Check Answer:** [44]

40. In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00 × 10^3 torr.

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

    a. How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
    b. Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

41. The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

   $$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

   a. On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapour, and 0.90 mol of H_2 in a litre. How many moles of CO_2 were there in the equilibrium mixture?
   b. Maintaining the same temperature, additional H_2 was added to the system, and some water vapour was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapour, and 1.2 mol of H_2 in a litre. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapour concentration to be the same in the two equilibrium solutions even though some vapour was removed before the second equilibrium was established. **Check Answer:** [45]

42. Antimony pentachloride decomposes according to this equation:

   $$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

   An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

43. Consider the reaction between H_2 and O_2 at 1000 K

   $$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K_P = \frac{(P_{H_2O})^2}{(P_{O_2})(P_{H_2})^3} = 1.33 \times 10^{20}$$

   If 0.500 atm of H_2 and 0.500 atm of O_2 are allowed to come to equilibrium at this temperature, what are the partial pressures of the components? **Check Answer:** [46]

44. An equilibrium is established according to the following equation

   $$Hg_2{}^{2+}(aq) + NO_3{}^-(aq) + 3H^+(aq) \rightleftharpoons 2Hg^{2+}(aq) + HNO_2(aq) + H_2O(l) \qquad K_c = 4.6$$

   What will happen in a solution that is 0.20 *M* each in $Hg_2{}^{2+}$, $NO_3{}^-$, H^+, Hg^{2+}, and HNO_2?

   a. $Hg_2{}^{2+}$ will be oxidized and $NO_3{}^-$ reduced.
   b. $Hg_2{}^{2+}$ will be reduced and $NO_3{}^-$ oxidized.
   c. Hg^{2+} will be oxidized and HNO_2 reduced.
   d. Hg^{2+} will be reduced and HNO_2 oxidized.
   e. There will be no change because all reactants and products have an activity of 1.

45. Consider the equilibrium

   $$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

   a. What is the expression for the equilibrium constant (K_c) of the reaction?
   b. How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
   c. If the reaction were at equilibrium, how would a decrease in pressure (from an increase in the volume of the reaction vessel) affect the pressure of NO_2?

d. If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change? **Check Answer:** [47]

46. The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$\mathrm{HbO_2}(aq)\ +\ \mathrm{H_3O^+}(aq)\ +\ \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2}\ -\ \mathrm{Hb}\ -\ \mathrm{H^+}\ +\ \mathrm{O_2}(g)\ +\ \mathrm{H_2O}(l)$$

    1. Write the equilibrium constant expression for this reaction.
    2. Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

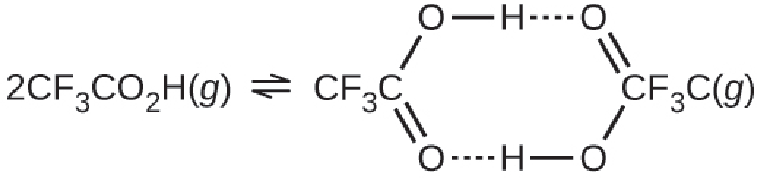
47. The hydrolysis of the sugar sucrose to the sugars glucose and fructose follows a first-order rate equation for the disappearance of sucrose.

$$\mathrm{C_{12}H_{22}O_{11}}(aq)\ +\ \mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(aq)\ +\ \mathrm{C_6H_{12}O_6}(aq)$$

Rate = $k[C_{12}H_{22}O_{11}]$

In neutral solution, $k = 2.1 \times 10^{-11}$/s at 27 °C. (As indicated by the rate constant, this is a very slow reaction. In the human body, the rate of this reaction is sped up by a type of catalyst called an enzyme.) (Note: That is not a mistake in the equation—the products of the reaction, glucose and fructose, have the same molecular formulas, $C_6H_{12}O_6$, but differ in the arrangement of the atoms in their molecules). The equilibrium constant for the reaction is 1.36×10^5 at 27 °C. What are the concentrations of glucose, fructose, and sucrose after a 0.150 M aqueous solution of sucrose has reached equilibrium? Remember that the activity of a solvent (the effective concentration) is 1. **Check Answer:** [48]

48. The density of trifluoroacetic acid vapour was determined at 118.1 °C and 468.5 torr, and found to be 2.784 g/L. Calculate K_c for the association of the acid shown in the figure below.



49. Liquid N_2O_3 is dark blue at low temperatures, but the colour fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of $K_P = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.
Check Answer: [49]

50. A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 M; H_2, 0.50 M; and NH_3, 0.25 M. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M?

51. A 0.010 M solution of the weak acid HA has an osmotic pressure (see chapter on solutions and colloids) of 0.293 atm at 25 °C. A 0.010 M solution of the weak acid HB has an osmotic pressure of 0.345 atm

under the same conditions.

a. Which acid has the larger equilibrium constant for ionization HA $[\mathrm{HA}(aq) \rightleftharpoons \mathrm{A}^-(aq)\ +\ \mathrm{H}^+(aq)]$ or HB $[\mathrm{HB}(aq) \rightleftharpoons \mathrm{H}^+(aq)\ +\ \mathrm{B}^-(aq)]$?

b. What are the equilibrium constants for the ionization of these acids?

(Hint: Remember that each solution contains three dissolved species: the weak acid (HA or HB), the conjugate base (A^- or B^-), and the hydrogen ion (H^+). Remember that osmotic pressure (like all colligative properties) is related to the total number of solute particles. Specifically for osmotic pressure, those concentrations are described by molarities.) **Check Answer:** [50]

17.6 Precipitation and Dissolution

1. Complete the changes in concentrations for each of the following reactions in the table below:

a.	$AgI_{(s)}$	→	$Ag^+_{(aq)}$	$+ I^-_{(aq)}$	
			x	______	
b.	$CaCO_{3\,(s)}$	→	$Ca^{2+}_{(aq)}$	$+ CO_3^{2-}{}_{(aq)}$	
			______	x	
c.	$Mg(OH)_{2\,(s)}$	→	$Mg^{2+}_{(aq)}$	$+ 2\,OH^-_{(aq)}$	
			x	______	
d.	$Mg_3(PO_4)_{2\,(s)}$	→	$3\,Mg^{2+}_{(aq)}$	$+ 2\,PO_4^{3-}{}_{(aq)}$	
			______	2x	
e.	$Ca_5(PO_4)_3OH_{(s)}$	→	$5\,Ca^{2+}_{(aq)}$	$+ 3\,PO_4^{3-}{}_{(aq)}$	$+ OH^-_{(aq)}$
			______	______	x

Check Answer: [51]

2. Complete the changes in concentrations for each of the following reactions in the table below:

a.	$BaSO_{4\,(s)}$	→	$Ba^{2+}{}_{(aq)}$	$+\ SO_4{}^{2-}{}_{(aq)}$	
			x	______	
b.	$Ag_2SO_{4\,(s)}$	→	$2\ Ag^{+}{}_{(aq)}$	$+\ SO_4{}^{2-}{}_{(aq)}$	
			______	x	
c.	$Al(OH)_{3\,(s)}$	→	$Al^{3+}{}_{(aq)}$	$+\ 3\ OH^{-}{}_{(aq)}$	
			x	______	
d.	$Pb(OH)Cl_{(s)}$	→	$Pb^{2+}{}_{(aq)}$	$+\ OH^{-}{}_{(aq)}$	$+\ Cl^{-}{}_{(aq)}$
			______	x	______
e.	$Ca_3(AsO_4)_{2\,(s)}$	→	$3\ Ca^{2+}{}_{(aq)}$	$+\ 2\ AsO_4{}^{3-}{}_{(aq)}$	
			3x	______	

3. How do the concentrations of Ag^+ and $CrO_4{}^{2-}$ in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain. **Check Answer:** [52]
4. How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS?
5. What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised? **Check Answer:** [53]
6. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?
7. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, ZnS, PbS? **Check Answer:** [54]
8. Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:
    a. $PbCl_2$
    b. Ag_2S
    c. $Sr_3(PO_4)_2$
    d. $SrSO_4$
9. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:
    a. LaF_3
    b. $CaCO_3$

   c. Ag_2SO_4
   d. $Pb(OH)_2$

   Check Answer: [55]

10. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.
    a. $BaSiF_6$, 0.026 g/100 mL (contains SiF_6^{2-} ions)
    b. $Ce(IO_3)_4$, 1.5×10^{-2} g/100 mL
    c. $Gd_2(SO_4)_3$, 3.98 g/100 mL
    d. $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains $PtBr_6^{2-}$ ions)
11. The *Handbook of Chemistry and Physics* gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.
    a. $BaSeO_4$, 0.0118 g/100 mL
    b. $Ba(BrO_3)_2{\cdot}H_2O$, 0.30 g/100 mL
    c. $NH_4MgAsO_4{\cdot}6H_2O$, 0.038 g/100 mL
    d. $La_2(MoO_4)_3$, 0.00179 g/100 mL

    Check Answer: [56]
12. Use solubility products and predict which of the following salts is the most soluble, in terms of moles per litre, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.
13. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:
    a. $KHC_4H_4O_6$
    b. PbI_2
    c. $Ag_4[Fe(CN)_6]$, a salt containing the $Fe(CN)_4^{-}$ ion
    d. Hg_2I_2

    Check Answer: [57]
14. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:
    a. Ag_2SO_4
    b. $PbBr_2$
    c. AgI
    d. $CaC_2O_4{\cdot}H_2O$
15. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.
    a. AgCl(*s*) in 0.025 *M* NaCl

   b. $CaF_2(s)$ in 0.00133 *M* KF
   c. $Ag_2SO_4(s)$ in 0.500 L of a solution containing 19.50 g of K_2SO_4
   d. $Zn(OH)_2(s)$ in a solution buffered at a pH of 11.45
      Check Answer: [58]

16. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.
    a. $TlCl(s)$ in 1.250 *M* HCl
    b. $PbI_2(s)$ in 0.0355 *M* CaI_2
    c. $Ag_2CrO_4(s)$ in 0.225 L of a solution containing 0.856 g of K_2CrO_4
    d. $Cd(OH)_2(s)$ in a solution buffered at a pH of 10.995
17. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.
    a. $TlCl(s)$ in 0.025 *M* $TlNO_3$
    b. $BaF_2(s)$ in 0.0313 *M* KF
    c. MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$
    d. $Ca(OH)_2(s)$ in an unbuffered solution initially with a pH of 12.700
       Check Answer: [59]
18. Calculate the solubility of aluminum hydroxide, $Al(OH)_3$, in a solution buffered at pH 11.00.
19. Refer to Appendix K for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per litre and which is most soluble in grams per litre. **Check Answer:** [60]
20. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract (Figure 17.6c). This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.
21. Public Health Service standards for drinking water set a maximum of 250 mg/L (2.60×10^{-3} *M*) of SO_4^{2-} because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ ("gyp" water) as a result or passing through soil containing gypsum, $CaSO_4{\cdot}2H_2O$, meet these standards? What is SO_4^{2-} in such water? **Check Answer:** [61]
22. Perform the following calculations:
    a. Calculate $[Ag^+]$ in a saturated aqueous solution of AgBr.
    b. What will $[Ag^+]$ be when enough KBr has been added to make $[Br^-] = 0.050$ *M*?
    c. What will $[Br^-]$ be when enough $AgNO_3$ has been added to make $[Ag^+] = 0.020$ *M*?
23. The solubility product of $CaSO_4{\cdot}2H_2O$ is 2.4×10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 *M* SO_4^{2-}? **Check Answer:** [62]
24. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a

saturated solution of each of the following (see Appendix K for solubility products).

  a. TlCl
  b. BaF_2
  c. Ag_2CrO_4
  d. $CaC_2O_4{\cdot}H_2O$
  e. the mineral anglesite, $PbSO_4$

25. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see Appendix K for solubility products):
    a. AgI
    b. Ag_2SO_4
    c. $Mn(OH)_2$
    d. $Sr(OH)_2{\cdot}8H_2O$
    e. the mineral brucite, $Mg(OH)_2$

    Check Answer: [63]
26. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:
    a. AgBr: $[Ag^+] = 5.7 \times 10^{-7} M$, $[Br^-] = 5.7 \times 10^{-7} M$
    b. $CaCO_3$: $[Ca^{2+}] = 5.3 \times 10^{-3} M$, $[CO_3^{2-}] = 9.0 \times 10^{-7} M$
    c. PbF_2: $[Pb^{2+}] = 2.1 \times 10^{-3} M$, $[F^-] = 4.2 \times 10^{-3} M$
    d. Ag_2CrO_4: $[Ag^+] = 5.3 \times 10^{-5} M$, $3.2 \times 10^{-3} M$
    e. InF_3: $[In^{3+}] = 2.3 \times 10^{-3} M$, $[F^-] = 7.0 \times 10^{-3} M$
27. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:
    a. TlCl: $[Tl^+] = 1.21 \times 10^{-2} M$, $[Cl^-] = 1.2 \times 10^{-2} M$
    b. $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8 \times 10^{-4} M$, $[IO_3^-] = 2.6 \times 10^{-13} M$
    c. $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132\ M$, $[SO_4^{2-}] = 0.198\ M$
    d. Ag_2SO_4: $[Ag^+] = 2.40 \times 10^{-2} M$, $[SO_4^{2-}] = 2.05 \times 10^{-2} M$
    e. $BaSO_4$: $[Ba^{2+}] = 0.500\ M$, $[SO_4^{2-}] = 2.16 \times 10^{-10} M$

    Check Answer: [64]
28. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix K for K_{sp} values.)
    a. $KClO_4$: $[K^+] = 0.01\ M$, $[ClO_4^-] = 0.01\ M$
    b. K_2PtCl_6: $[K^+] = 0.01\ M$, $[PtCl_6^{2-}] = 0.01\ M$
    c. PbI_2: $[Pb^{2+}] = 0.003\ M$, $[I^-] = 1.3 \times 10^{-3} M$
    d. Ag_2S: $[Ag^+] = 1 \times 10^{-10} M$, $[S^{2-}] = 1 \times 10^{-13} M$
29. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See Appendix K for K_{sp} values.)

   a. $CaCO_3$: $[Ca^{2+}] = 0.003\ M$, $[CO_3^{2-}] = 0.003\ M$
   b. $Co(OH)_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1 \times 10^{-7} M$
   c. $CaHPO_4$: $[Ca^{2+}] = 0.01\ M$, $[HPO_4^{2-}] = 2 \times 10^{-6} M$
   d. $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01\ M$, $[PO_4^{3-}] = 1 \times 10^{-13} M$
   Check Answer: [65]

30. Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^-.
31. Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 M in Ba^{2+}. **Check Answer:** [66]
32. Calculate the concentration of Sr^{2+} when SrF_2 starts to precipitate from a solution that is 0.0025 M in F^-.
33. Calculate the concentration of PO_4^{3-} when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+. **Check Answer:** [67]
34. Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 M in Ca^{2+}.
35. Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is $2.50 \times 10^{-6} M$ in CO_3^{2-}. **Check Answer:** [68]
36. What $[Ag^+]$ is required to reduce $[CO_3^{2-}]$ to $8.2 \times 10^{-4} M$ by precipitation of Ag_2CO_3?
37. What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0 \times 10^{-4} M$ by precipitation of CaF_2? **Check Answer:** [69]
38. A volume of 0.800 L of a 2×10^{-4}–M $Ba(NO_3)_2$ solution is added to 0.200 L of $5 \times 10^{-4} M$ Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.
39. Perform these calculations for nickel(II) carbonate.
   a. With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36 \times 10^{-7}$).
   b. If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.
   Check Answer: [70]
40. Iron concentrations greater than $5.4 \times 10^{-6} M$ in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?
41. A solution is 0.010 M in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide? **Check Answer:** [71]
42. A solution is 0.15 M in both Pb^{2+} and Ag^+. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?
43. What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 M with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in Appendix K.)

  a. Hg_2^{2+} and Cu^{2+}
  b. SO_4^{2-} and Cl^-
  c. Hg^{2+} and Co^{2+}
  d. Zn^{2+} and Sr^{2+}
  e. Ba^{2+} and Mg^{2+}
  f. CO_3^{2-} and OH^-

  Check Answer: [72]

44. A solution contains 1.0 × 10^{-5} mol of KBr and 0.10 mol of KCl per litre. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?
45. A solution contains 1.0 × 10^{-2} mol of KI and 0.10 mol of KCl per litre. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl? **Check Answer:** [73]
46. The calcium ions in human blood serum are necessary for coagulation. Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4{\cdot}H_2O$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)
47. About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form? **Check Answer:** [74]
48. The pH of normal urine is 6.30, and the total phosphate concentration $[PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$ is 0.020 M. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation?
49. Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

$$\text{Mg}^{2+}(aq) + \text{Ca(OH)}_2(aq) \longrightarrow \text{Mg(OH)}_2(s) + \text{Ca}^{2+}(aq)$$
$$\text{Mg(OH)}_2(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(s) + 2\text{H}_2\text{O}(l)$$
$$\text{MgCl}_2(l) \xrightarrow{\text{electrolysis}} \text{Mg}(s) + \text{Cl}_2(g)$$

    Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00 × 10^3 L of sea water? **Check Answer:** [75]
50. Hydrogen sulfide is bubbled into a solution that is 0.10 M in both Pb^{2+} and Fe^{2+} and 0.30 M in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[H_2S] = 0.10\ M$). What

concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

$$\mathrm{H_2S}(aq) \;+\; 2\mathrm{H_2O}(l) \rightleftharpoons 2\mathrm{H_3O^+}(aq) \;+\; \mathrm{S^{2-}}(aq) \qquad K = 1.0 \;\times\; 10^{-26}$$

(Hint: The $[H_3O^+]$ changes as metal sulfides precipitate.)

51. Perform the following calculations involving concentrations of iodate ions:
    a. The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1×10^{-3} mol/L. Find the K_{sp}.
    b. Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ ($K_{sp} = 7.4 \times 10^{-8}$).
    Check Answer: [76]
52. Calculate the molar solubility of AgBr in 0.035 M NaBr ($K_{sp} = 5 \times 10^{-13}$).
53. How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-M $PbCl_2$ solution ($K_{sp} = 1.2 \times 10^{-15}$)? **Check Answer:** [77]
54. How many grams of Milk of Magnesia, $Mg(OH)_2$ (*s*) (58.3 g/mol), would be soluble in 200 mL of water. $K_{sp} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)
55. Two hypothetical salts, LM_2 and LQ, have the same molar solubility in H_2O. If K_{sp} for LM_2 is 3.20×10^{-5}, what is the K_{sp} value for LQ? **Check Answer:** [78]
56. Which of the following carbonates will form first? Which of the following will form last? Explain.
    a. $\mathrm{MgCO_3} \qquad K_{\mathrm{sp}} = 3.5 \;\times\; 10^{-8}$
    b. $\mathrm{CaCO_3} \qquad K_{\mathrm{sp}} = 4.2 \;\times\; 10^{-7}$
    c. $\mathrm{SrCO_3} \qquad K_{\mathrm{sp}} = 3.9 \;\times\; 10^{-9}$
    d. $\mathrm{BaCO_3} \qquad K_{\mathrm{sp}} = 4.4 \;\times\; 10^{-5}$
    e. $\mathrm{MnCO_3} \qquad K_{\mathrm{sp}} = 5.1 \;\times\; 10^{-9}$
    Check Answer: [79]
57. How many grams of $Zn(CN)_2$(*s*) (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2$(*s*) is 3.0×10^{-16}.

17.7 Relative Strengths of Acids and Bases

1. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.
2. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.
   Check Answer: [80]
3. Use this list of important industrial compounds (and Figure 17.7c) 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 (a) that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.
   c. List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

4. The odour 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. **Check Answer:** [81]
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.
6. Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3. **Check Answer:** [82]
7. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.
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. **Check Answer:** [83]
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.
10. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$. **Check Answer:** [84]
11. What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?
12. Which base, CH_3NH_2 or $(CH_3)_2NH$, is the stronger base? Which conjugate acid, $(CH_3)_2NH_2^+$ or $(CH_3)_2NH$, is the stronger acid? **Check Answer:** [85]
13. Which is the stronger acid, NH_4^+ or HBrO?
14. Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3^-$? **Check Answer:** [86]
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. HSO_3^- or HSO_4^-
    d. NH_3 or H_2S
    e. H_2O or H_2Te
16. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

   a. HSO_4^- or $HSeO_4^-$
   b. NH_3 or H_2O
   c. PH_3 or HI
   d. NH_3 or PH_3
   e. H_2S or HBr
   Check Answer: [87]
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
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: BrO_2^-, ClO_2^-, IO_2^-
   c. acidity: HOCl, HOBr, HOI
   d. acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$
   e. basicity: NH_2^-, HS^-, HTe^-, PH_2^-
   f. basicity: BrO^-, BrO_2^-, BrO_3^-, BrO_4^-
   Check Answer: [88]
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 17.7b.
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 $C_6H_4OH(CO_2H)$. **Check Answer:** [89]
21. What do we represent when we write:
   $$\mathrm{CH_3CO_2H}(aq) \ + \ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) \ + \ \mathrm{CH_3CO_2}^-(aq)?$$
22. 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? **Check Answer:** [90]
23. 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.
24. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid? **Check Answer:** [91]

25. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak base?
26. 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
    Check Answer: [92]
27. 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
28. What is the effect on the concentrations of 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:
    $$\mathrm{NO_2}^-(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HNO_2}(aq)\ +\ \mathrm{OH}^-(aq)$$
    Check Answer: [93]
29. 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:$\mathrm{HF}(aq)\ +\ \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq)\ +\ \mathrm{F}^-(aq)$
30. 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? **Check Answer:** [94]
31. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.
    a. CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3} M$;
    $[CH_3CO_2^-] = 1.34 \times 10^{-3} M$;
    $[CH_3CO_2H] = 9.866 \times 10^{-2} M$;

   b. ClO^-: $[OH^-] = 4.0 \times 10^{-4} M$;
   $[HClO] = 2.38 \times 10^{-5} M$;
   $[ClO^-] = 0.273\,M$;

   c. HCO_2H: $[HCO_2H] = 0.524\,M$;
   $[H_3O^+] = 9.8 \times 10^{-3} M$;
   $[HCO_2^-] = 9.8 \times 10^{-3} M$;

   d. $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233\,M$;
   $[C_6H_5NH_2] = 2.3 \times 10^{-3} M$;
   $[H_3O^+] = 2.3 \times 10^{-3} M$

32. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.
   a. NH_3: $[OH^-] = 3.1 \times 10^{-3} M$;
   $[NH_4^+] = 3.1 \times 10^{-3} M$;
   $[NH_3] = 0.533\,M$;

   b. HNO_2: $[H_3O^+] = 0.011\,M$;
   $[NO_2^-] = 0.0438\,M$;
   $[HNO_2] = 1.07\,M$;

   c. $(CH_3)_3N$: $[(CH_3)_3N] = 0.25\,M$;
   $[(CH_3)_3NH^+] = 4.3 \times 10^{-3} M$;
   $[OH^-] = 4.3 \times 10^{-3} M$;

   d. NH_4^+: $[NH_4^+] = 0.100\,M$;
   $[NH_3] = 7.5 \times 10^{-6} M$;
   $[H_3O^+] = 7.5 \times 10^{-6} M$
   Check Answer: [95]

33. Determine K_b for the nitrite ion, NO_2^-. In a 0.10-M solution this base is 0.0015% ionized.
34. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-M solution the acid is 29% ionized. **Check Answer:** [96]
35. 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. NH_4^+
   c. AsO_4^{3-}
   d. $(CH_3)_2NH_2^+$

   e. NO_2^-
   f. $HC_2O_4^-$ (as a base)
36. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:
   a. HTe^- (as a base)
   b. $(CH_3)_3NH^+$
   c. $HAsO_4^{3-}$ (as a base)
   d. HO_2^- (as a base)
   e. $C_6H_5NH_3^+$
   f. HSO_3^- (as a base)

   Check Answer: [97]
37. For which of the following solutions must we consider the ionization of water when calculating the pH or pOH?
   a. $3 \times 10^{-8} M$ 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. $1 \times 10^{-7} M$ $Ca(OH)_2$
   e. 0.0245 *M* KNO_3
38. 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

   Check Answer: [98]
39. 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.
40. 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. **Check Answer:** [99]
41. 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 ($K_b = 1.7 \times 10^{-9}$).
42. 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 $C_6H_5NH_2$. **Check Answer:** [100]
43. Using the K_a value of 1.4×10^{-5}, place $Al(H_2O)_6^{3+}$ in the correct location in Figure 17.7c.

44. 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 I and Appendix J.
    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* $FeH_2O_6{}^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$
    Check Answer: [101]
45. 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 $C_2H_5CO_2H$?
46. 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? **Check Answer:** [102]
47. 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?
48. 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? **Check Answer:** [103]
49. The pH of a 0.20-*M* solution of HF is 1.92. Determine K_a for HF from these data.
50. The pH of a 0.15-*M* solution of $HSO_4{}^-$ is 1.43. Determine K_a for $HSO_4{}^-$ from these data. **Check Answer:** [104]
51. The pH of a 0.10-*M* solution of caffeine is 11.16. Determine K_b for caffeine from these data:
    $$C_8H_{10}N_4O_2(aq) + H_2O(l) \leftrightharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$
52. 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. **Check Answer:** [105]

17.8 Real World Examples of Equilibria

1. A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?
2. Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$. **Check Answer:** [106]
3. Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of $Zn(CN)_4{}^{2-}$.
4. Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3. **Check Answer:** [107]
5. Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^-.

6. Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 *M* CN^-. **Check Answer:** [108]
7. Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.025 *M* NH_3. Assume the volume is 1.00 L.
8. The equilibrium constant for the reaction $\mathrm{Hg}^{2+}(aq) + 2\mathrm{Cl}^-(aq) \leftrightharpoons \mathrm{HgCl}_2(aq)$ is 1.6×10^{13}. Is $HgCl_2$ a strong electrolyte or a weak electrolyte? What are the concentrations of Hg^{2+} and Cl^- in a 0.015-*M* solution of $HgCl_2$? **Check Answer:** [109]
9. Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and NH_4^+.
10. Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 *M* NH_3 and 0.400 *M* NH_4^+. **Check Answer:** [110]
11. What is the molar solubility of CaF_2 in a 0.100-*M* solution of HF? K_a for HF = 7.2×10^{-4}.
12. What is the molar solubility of $BaSO_4$ in a 0.250-*M* solution of $NaHSO_4$? K_a for HSO_4^- = 1.2×10^{-2}. **Check Answer:** [111]
13. What is the molar solubility of $Tl(OH)_3$ in a 0.10-*M* solution of NH_3?
14. What is the molar solubility of $Pb(OH)_2$ in a 0.138-*M* solution of CH_3NH_2? **Check Answer:** [112]
15. A solution of 0.075 *M* $CoBr_2$ is saturated with H_2S ($[H_2S]$ = 0.10 *M*). What is the minimum pH at which CoS begins to precipitate?

    $$\mathrm{CoS}(s) \leftrightharpoons \mathrm{Co}^{2+}(aq) + \mathrm{S}^{2-}(aq) \qquad K_{\mathrm{sp}} = 4.5 \times 10^{-27}$$

    $$\mathrm{H_2S}(aq) + 2\mathrm{H_2O}(l) \leftrightharpoons 2\mathrm{H_3O}^+(aq) + \mathrm{S}^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$
16. A 0.125-*M* solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S]$ = 0.10 *M*). At what pH does MnS begin to precipitate?

    $$\mathrm{MnS}(s) \rightleftharpoons \mathrm{Mn}^{2+}(aq) + \mathrm{S}^{2-}(aq) \qquad K_{\mathrm{sp}} = 4.3 \times 10^{-22}$$

    $$\mathrm{H_2S}(aq) + 2\mathrm{H_2O}(l) \rightleftharpoons 2\mathrm{H_3O}^+(aq) + \mathrm{S}^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$

    Check Answer: [113]
17. Calculate the molar solubility of BaF_2 in a buffer solution containing 0.20 *M* HF and 0.20 *M* NaF.
18. Calculate the molar solubility of $CdCO_3$ in a buffer solution containing 0.115 *M* Na_2CO_3 and 0.120 *M* $NaHCO_3$ **Check Answer:** [114]
19. To a 0.10-*M* solution of $Pb(NO_3)_2$ is added enough HF(*g*) to make [HF] = 0.10 *M*.
    a. Does PbF_2 precipitate from this solution? Show the calculations that support your conclusion.
    b. What is the minimum pH at which PbF_2 precipitates?
20. Calculate the concentration of Cd^{2+} resulting from the dissolution of $CdCO_3$ in a solution that is 0.010 *M* in H_2CO_3. **Check Answer:** [115]
21. Both AgCl and AgI dissolve in NH_3.
    a. What mass of AgI dissolves in 1.0 L of 1.0 *M* NH_3?
    b. What mass of AgCl dissolves in 1.0 L of 1.0 *M* NH_3?
22. Calculate the volume of 1.50 *M* CH_3CO_2H required to dissolve a precipitate composed of 350 mg each

of $CaCO_3$, $SrCO_3$, and $BaCO_3$. **Check Answer:** [116]

23. Even though $Ca(OH)_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $Ca(OH)_2$?
24. What mass of NaCN must be added to 1 L of 0.010 M $Mg(NO_3)_2$ in order to produce the first trace of $Mg(OH)_2$? **Check Answer:** [117]
25. Magnesium hydroxide and magnesium citrate function as mild laxatives when they reach the small intestine. Why do magnesium hydroxide and magnesium citrate, two very different substances, have the same effect in your small intestine. (Hint: The contents of the small intestine are basic.)
26. The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.
    Solve the following problem:

    $$\text{MgF}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{F}^-(aq)$$

    In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is $1.21 \times 10^{-3} M$. The equilibrium is represented by the preceding equation.
    1. Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.
    2. Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.
    3. Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00×10^{-3}–M solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00×10^{-3}–M solution of NaF at 18 °C. Show the calculations to support your prediction.
    4. At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is $1.17 \times 10^{-3} M$. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.
       Check Answer: [118]
27. Which of the following compounds, when dissolved in a 0.01-M solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.
28. Which of the following compounds, when dissolved in a 0.01-M solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_3$, ZnS, PbI_2? Explain your answer. **Check Answer:** [119]
29. What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ and water at equilibrium?
    - a. $MgCl_2$
    - b. KOH
    - c. $HClO_4$
    - d. $NaNO_3$

   e. $Mg(OH)_2$

30. What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and HPO_4^{-} when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?
    a. $CaCl_2$
    b. HCl
    c. $KClO_4$
    d. NaOH
    e. $CaHPO_4$

    Check Answer: [120]
31. Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the PO_4^{3-} ion is a weak base.)
32. A volume of 50 mL of 1.8 *M* NH_3 is mixed with an equal volume of a solution containing 0.95 g of $MgCl_2$. What mass of NH_4Cl must be added to the resulting solution to prevent the precipitation of $Mg(OH)_2$? **Check Answer:** [121]

Attribution & References

Except where otherwise noted, this page is adapted by David Wegman from "12.1 Chemical Reaction Rates", "13.1 Chemical Equilibria", "13.2 Equilibrium Constants", "13.3 Shifting Equilibria: Le Chatelier's Principle", "13.4 Equilibrium Calculations", "14.3 Strengths of Acids and Bases" (https://boisestate.pressbooks.pub/chemistry/chapter/14-3-relative-strengths-of-acids-and-bases/), "15.1 Precipitation and Dissolution" and "15.3 Coupled Equilibria (https://boisestate.pressbooks.pub/chemistry/chapter/15-3-coupled-equilibria/)" In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax) (https://openstax.org/books/chemistry/pages/1-introduction)* . / End of chapter exercises extracted and reused.

Notes

1. The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.
2. $$\text{rate} = +\frac{1}{2}\frac{\Delta[\mathrm{CIF_3}]}{\Delta t} = -\frac{\Delta[\mathrm{Cl_2}]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\mathrm{F_2}]}{\Delta t}$$
3. (a) average rate, 0 – 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 12 – 18 s = 0.0225 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.0500 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation =

$0.0250 \text{ mol L}^{-1} \text{ s}^{-1}$

4. The reaction can proceed in both the forward and reverse directions.
5. When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.
6. The concept of equilibrium does not imply equal concentrations, though it is possible.
7. Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.
8. (a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*; (b) $K_c = \frac{1}{[Pb^{2+}][Cl^-]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).
9. Since $K_c = \frac{[C_6H_6]}{[C_2H_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.
10. $K_c > 1$
11. (a) $Q_c = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \frac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) $Q_c = [SO_2]$; (e) $Q_c = \frac{1}{[P_4][O_2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br_2]}$; (g) $Q_c = \frac{[CO_2]}{[CH_4][O_2]^2}$; (h) $Q_c = [H_2O]^5$
12. (a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left
13. The system will shift toward the reactants to reach equilibrium.
14. (a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$
15. $K_P = P_{H_2O} = 0.042$.
16. $Q_c = \frac{[NH_4{}^+][OH^-]}{[NH_3]}$
17. The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.
18. The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.
19. No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.
20. Add N_2; add H_2; decrease the container volume; heat the mixture.

21. (a) $K_c = \frac{[CO][H_2]}{[H_2O]}$; (b) $[H_2O]$ no change, [CO] no change, $[H_2]$ no change; (c) $[H_2O]$ decreases, [CO] decreases, $[H_2]$ decreases; (d) $[H_2O]$ increases, [CO] increases, $[H_2]$ decreases; (f) $[H_2O]$ decreases, [CO] increases, $[H_2]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.
22. Only (b)
23. Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(*s*).
24. (a)
25. $K_c = \frac{[C]^2}{[A][B]^2}$. [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.
26. $K_c = 6.00 \times 10^{-2}$
27. $K_c = 0.50$
28. The equilibrium equation is $K_P = 1.9 \times 10^3$
29. $K_P = 3.06$
30. (a) $-2x$, $2x$, -0.250 *M*, 0.250 *M*; (b) $4x$, $-2x$, $-6x$, 0.32 *M*, -0.16 *M*, -0.48 *M*; (c) $-2x$, $3x$, -50 torr, 75 torr; (d) x, $-x$, $-3x$, 5 atm, -5 atm, -15 atm; (e) x, 1.03×10^{-4} *M*; (f) x, 0.1 atm.
31. Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.
32. $[NH_3] = 9.1 \times 10^{-2} M$
33. $P_{BrCl} = 4.9 \times 10^{-2}$ atm
34. $[CO] = 2.0 \times 10^{-4} M$
35. $P_{H_2O} = 3.64 \times 10^{-3}$ atm
36. Calculate *Q* based on the calculated concentrations and see if it is equal to K_c. Because *Q* does equal 4.32, the system must be at equilibrium.
37. (a) $[NO_2] = 1.17 \times 10^{-3} M$; $[N_2O_4] = 0.128 M$ (b) Percent error $= \frac{5.87 \times 10^{-4}}{0.129} \times 100\% = 0.455\%$. The change in concentration of N_2O_4 is far less than the 5% maximum allowed.
38. (a) $[H_2S] = 0.810$ atm ; $[H_2] = 0.014$ atm ; $[S_2] = 0.0072$ atm (b) The $2x$ is dropped from the equilibrium calculation because 0.014 is negligible when subtracted from 0.824. The percent error associated with ignoring $2x$ is $\frac{0.014}{0.824} \times 100\% = 1.7\%$, which is less than allowed by the "5% test." The error is, indeed, negligible.
39. $[PCl_3] = 1.80 M$; $[PC_3] = 0.195 M$; $[PCl_3] = 0.195 M$.
40. $[NO_2] = 0.19 M$; $[NO] = 0.0070 M$; $[O_2] = 0.0035 M$
41. $P_{O_3} = 4.9 \times 10^{-26}$ atm
42. 507 g
43. 330 g
44. (a) Both gases must increase in pressure. (b) $P_{N_2O_4} = 8.0$ atm and $P_{NO_2} = 1.0$ atm
45. (a) 0.33 mol. (b) $[CO]^2 = 0.50 M$ Added H_2 forms some water to compensate for the removal of water vapour and as a result of a shift to the left after H_2 is added.

46. $P_{\mathrm{H_2}} = 8.64 \times 10^{-11}\ \mathrm{atm}\ P_{\mathrm{O_2}} = 0.250\ \mathrm{atm}\ P_{\mathrm{H_2O}} = 0.500\ \mathrm{atm}$

47. (a) $K_c = \dfrac{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}$. (b) $[\mathrm{NH_3}]$ must increase for Q_c to reach K_c. (c) That decrease in pressure would decrease $[\mathrm{NO_2}]$. (d) $P_{\mathrm{O_2}} = 49\ \mathrm{torr}$

48. [fructose] = 0.15 M

49. $P_{\mathrm{N_2O_3}} = 1.90\ \mathrm{atm\ and}\ P_{\mathrm{NO}} = P_{\mathrm{NO_2}} = 1.90\ \mathrm{atm}$

50. (a) HB ionizes to a greater degree and has the larger K_c. (b) $K_c(\mathrm{HA}) = 5 \times 10^{-4}$ $K_c(\mathrm{HB}) = 3 \times 10^{-3}$

51. (a)

$$\begin{array}{ccccc} \mathrm{AgI}(s) \rightleftharpoons & \mathrm{Ag}^+(aq) & + & \mathrm{I}^-(aq) \\ & x & & \underline{x} \end{array}$$

(b)

$$\begin{array}{ccccc} \mathrm{CaCO_3}(s) \rightleftharpoons & \mathrm{Ca}^{2+}(aq) & + & \mathrm{CO_3}^{2-}(aq) \\ & \underline{x} & & x \end{array}$$

(c)

$$\begin{array}{ccccc} \mathrm{Mg(OH)_2}(s) \rightleftharpoons & \mathrm{Mg}^{2+}(aq) & + & 2\mathrm{OH}^-(aq) \\ & x & & \underline{2x} \end{array}$$

(d)

$$\begin{array}{ccccc} \mathrm{Mg_3(PO_4)_2}(s) \rightleftharpoons & 3\mathrm{Mg}^{2+}(aq) & + & 2\mathrm{PO_4}^{3-}(aq) \\ & \underline{3x} & & 2x \end{array}$$

(e)

$$\begin{array}{ccccccc} \mathrm{Ca_5(PO_4)_3OH}(s) \rightleftharpoons & 5\mathrm{Ca}^{2+}(aq) & + & 3\mathrm{PO_4}^{3-}(aq) & + & \mathrm{OH}^-(aq) \\ & \underline{5x} & & \underline{3x} & & x \end{array}$$

52. There is no change. A solid has an activity of 1 whether there is a little or a lot.

53. The solubility of silver bromide at the new temperature must be known. Normally the solubility increases and some of the solid silver bromide will dissolve.

54. $\mathrm{CaF_2}$, $\mathrm{MnCO_3}$, and ZnS

55. (a) $\mathrm{LaF_3}(s) \rightleftharpoons \mathrm{La}^{3+}(aq) + 3\mathrm{F}^-(aq) \qquad K_{\mathrm{sp}} = [\mathrm{La}^{3+}][\mathrm{F}^-]^3$; (b)
$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{CO_3}^{2-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{CO_3}^{2-}]$; (c)
$\mathrm{Ag_2SO_4}(s) \rightleftharpoons 2\mathrm{Ag}^+(aq) + \mathrm{SO_4}^{2-}(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Ag}^+]^2[\mathrm{SO_4}^{2-}]$; (d)
$\mathrm{Pb(OH)_2}(s) \rightleftharpoons \mathrm{Pb}^{2+}(aq) + 2\mathrm{OH}^-(aq) \qquad K_{\mathrm{sp}} = [\mathrm{Pb}^{2+}][\mathrm{OH}^-]^2$

56. (a) 1.77×10^{-7}; (b) 1.6×10^{-6}; (c) 2.2×10^{-9}; (d) 7.91×10^{-22}

57. (a) $2 \times 10^{-2} M$; (b) $1.5 \times 10^{-3} M$; (c) $2.27 \times 10^{-9} M$; (d) $2.2 \times 10^{-10} M$

58. (a) $6.4 \times 10^{-9} M = [\mathrm{Ag}^+]$, $[\mathrm{Cl}^-] = 0.025\ M$ Check: $\dfrac{6.4 \times 10^{-9}\ M}{0.025\ M} \times 100\% = 2.6 \times 10^{-5}$,an insignificant change; (b) $2.2 \times 10^{-5} M = [\mathrm{Ca}^{2+}]$, $[\mathrm{F}^-] = 0.0013\ M$ Check: $\dfrac{2.26 \times 10^{-5}\ M}{0.00133\ M} \times 100\% = 1.70\%$. This value is less than 5% and can be ignored. (c) $0.2238\ M = [\mathrm{SO_4}^{2-}]$; $[\mathrm{Ag}^+] = 7.4 \times 10^{-3} M$ Check: $\dfrac{3.7 \times 10^{-3}}{0.2238} \times 100\% = 1.64 \times 10^{-2}\%$; the condition is satisfied. (d) $[\mathrm{OH}^-] = 2.8 \times 10^{-3} M$; $5.7 \times 10^{-12} M = [\mathrm{Zn}^{2+}]$ Check:

$\dfrac{5.7 \times 10^{-12}}{2.8 \times 10^{-3}} \times 100\% = 2.0 \times 10^{-7}\%$; x is less than 5% of $[OH^-]$ and is, therefore, negligible.

59. (a) $[Cl^-] = 7.6 \times 10^{-3} M$ Check: $\dfrac{7.6 \times 10^{-3}}{0.025} \times 100\% = 30\%$ This value is too large to drop x. Therefore solve by using the quadratic equation: $[Ti^+] = 3.1 \times 10^{-2} M$ $[Cl^-] = 6.1 \times 10^{-3}$
(b) $[Ba^{2+}] = 7.7 \times 10^{-4} M$ Check: $\dfrac{7.7 \times 10^{-4}}{0.0313} \times 100\% = 2.4\%$ Therefore, the condition is satisfied. $[Ba^{2+}] = 7.7 \times 10^{-4} M$ $[F^-] = 0.0321\ M$; (c) $Mg(NO_3)_2 = 0.02444\ M$ $[C_2O_4{}^{2-}] = 2.9 \times 10^{-5}$ Check: $\dfrac{2.9 \times 10^{-5}}{0.02444} \times 100\% = 0.12\%$ The condition is satisfied; the above value is less than 5%. $[C_2O_4{}^{2-}] = 2.9 \times 10^{-5}\ M$ $[Mg^{2+}] = 0.0244\ M$ (d) $[OH^-] = 0.0501\ M$ $[Ca^{2+}] = 3.15 \times 10^{-3}$ Check: $\dfrac{3.15 \times 10^{-3}}{0.050} \times 100\% = 6.28\%$ This value is greater than 5%, so a more exact method, such as successive approximations, must be used. $[Ca^{2+}] = 2.8 \times 10^{-3} M$ $[OH^-] = 0.053 \times 10^{-2} M$
60. $CaSO_4{\cdot}2H_2O$ is the most soluble Ca salt in mol/L, and it is also the most soluble Ca salt in g/L.
61. $4.8 \times 10^{-3} M = [SO_4{}^{2-}] = [Ca^{2+}]$; Since this concentration is higher than $2.60 \times 10^{-3} M$, “gyp” water does not meet the standards.
62. Mass $(CaSO_4{\cdot}2H_2O) = 0.72$ g/L
63. (a) $[Ag^+] = [I^-] = 1.3 \times 10^{-5} M$; (b) $[Ag^+] = 2.88 \times 10^{-2} M$, $[SO_4{}^{2-}] = 1.44 \times 10^{-2} M$; (c) $[Mn^{2+}] = 3.7 \times 10^{-5} M$, $[OH^-] = 7.4 \times 10^{-5} M$; (d) $[Sr^{2+}] = 4.3 \times 10^{-2} M$, $[OH^-] = 8.6 \times 10^{-2} M$; (e) $[Mg^{2+}] = 1.3 \times 10^{-4} M$, $[OH^-] = 2.6 \times 10^{-4} M$.
64. (a) 2.0×10^{-4}; (b) 5.1×10^{-17}; (c) 1.35×10^{-4}; (d) 1.18×10^{-5}; (e) 1.08×10^{-10}
65. (a) $CaCO_3$ does precipitate. (b) The compound does not precipitate. (c) The compound does not precipitate. (d) The compound precipitates.
66. $3.03 \times 10^{-7} M$
67. $9.2 \times 10^{-13} M$
68. $[Ag^+] = 1.8 \times 10^{-3} M$
69. 6.3×10^{-4}
70. (a) 2.25 L; (b) 7.2×10^{-7} g
71. 100% of it is dissolved
72. (a) $Hg_2{}^{2+}$ and Cu^{2+}: Add $SO_4{}^{2-}$. (b) $SO_4{}^{2-}$ and Cl^-: Add Ba^{2+}. (c) Hg^{2+} and Co^{2+}: Add S^{2-}. (d) Zn^{2+} and Sr^{2+}: Add OH^- until $[OH^-] = 0.050\ M$. (e) Ba^{2+} and Mg^{2+}: Add $SO_4{}^{2-}$. (f) $CO_3{}^{2-}$ and OH^-: Add Ba^{2+}.
73. AgI will precipitate first.
74. $1.5 \times 10^{-12} M$
75. 3.99 kg
76. (a) 3.1×10^{-11}; (b) $[Cu^{2+}] = 2.6 \times 10^{-3}$; $[IO_3{}^-] = 5.3 \times 10^{-3}$
77. 1.8×10^{-5} g $Pb(OH)_2$

78. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^- \qquad K_{sp} = [Mg^{2+}][OH^-]^2$
1.23×10^{-3} g $Mg(OH)_2$

79. $MnCO_3$ will form first, since it has the smallest K_{sp} value it is the least soluble. $MnCO_3$ will be the last to precipitate, it has the largest K_{sp} value.

80. 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.

81. $[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2{}^-] > [OH^-]$

82. The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

83. $$\underset{\text{BB}}{Mg(OH)_2(s)} + \underset{\text{BA}}{2HCl(aq)} \longrightarrow \underset{\text{CB}}{Mg^{2+}(aq)} + \underset{\text{CA}}{2Cl^-(aq)} + 2H_2O(l)$$ holy

84. $K_a = 2.3 \times 10^{-11}$

85. The stronger base or stronger acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3{}^+$.

86. triethylamine.

87. (a) $HSO_4{}^-$; higher electronegativity of the central ion. (b) H_2O; NH_3 is a base and water is neutral, or decide on the basis of K_a values. (c) HI; 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.

88. (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) $ClO_2{}^- < BrO_2{}^- < IO_2{}^-$; 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) $HTe^- < HS^- \ll PH_2{}^- < NH_2{}^-$; $PH_2{}^-$ and $NH_2{}^-$ are anions of weak bases, so they act as strong bases toward H^+. 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) $BrO_4{}^- < BrO_3{}^- < BrO_2{}^- < BrO^-$; 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.

89. $[H_2O] > [C_6H_4OH(CO_2H)] > [H^+]_0 > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]$

90. 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.

91. 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^+.

92. (b) The addition of HCl

93. (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 $NO_2{}^-$ ions. (b) Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of $NO_2{}^-$ 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 $NO_2{}^-$ 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 $NO_2{}^-$ ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

94. 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.

95. (a) $K_b = 1.8 \times 10^{-5}$; (b) $K_a = 4.5 \times 10^{-4}$; (c) $K_b = 7.4 \times 10^{-5}$; (d) $K_a = 5.6 \times 10^{-10}$

96. $K_a = 1.2 \times 10^{-2}$

97. (a) $K_b = 4.3 \times 10^{-12}$; (b) $K_a = 1.6 \times 10^{-8}$; (c) $K_b = 5.9 \times 10^{-7}$; (d) $K_b = 4.2 \times 10^{-3}$; (e) $K_b = 2.3 \times 10^{-3}$; (f) $K_b = 6.3 \times 10^{-13}$

98. (a) is the correct statement.

99. $[H_3O^+] = 7.5 \times 10^{-3} M$ $[HNO_2] = 0.127$ $[OH^-] = 1.3 \times 10^{-12} M$ $[BrO^-] = 4.5 \times 10^{-8} M$ $[HBrO] = 0.120 M$

100. $[OH^-] = [NO_4{}^+] = 0.0014 M$ $[NH_3] = 0.144 M$ $[H_3O^+] = 6.9 \times 10^{-12} M$ $[C_6H_5NH_3{}^+] = 3.9 \times 10^{-8} M$ $[C_6H_5NH_2] = 0.100 M$

101. (a) $\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$ Solving for *x* gives $1.63 \times 10^{-5} M$. 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: $[H_3O^+] = [ClO] = 5.8 \times 10^{-5} M$ $[HClO] = 0.00092 M$ $[OH^-] = 6.1 \times 10^{-10} M$; (b) $\frac{[C_6H_5NH_3{}^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$ Solving for *x* gives $5.81 \times 10^{-6} M$. 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: $[CH_3CO_2{}^-] = [OH^-] = 5.8 \times 10^{-6} M$ $[C_6H_5NH_2] = 0.00784$ $[H_3O^+] = 1.7 \times 10^{-9} M$;(c) $\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$ Solving for *x* gives $6.30 \times 10^{-6} M$. 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: $[H_3O^+] = [CN^-] = 6.3 \times 10^{-6} M$ $[HCN] = 0.0810 M$ $[OH^-] = 1.6 \times 10^{-9} M$;(d) $\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$ Solving for *x* gives $2.63 \times 10^{-3} M$. 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: $[(CH_3)_3NH^+] = [OH^-] = 2.6 \times 10^{-3} M$ $[(CH_3)_3N] = 0.11 M$

$[H_3O^+] = 3.8 \times 10^{-12} M$;(e) $\dfrac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6{}^{2+}]} = \dfrac{(x)(x)}{(0.120 - x)} \approx \dfrac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$
Solving for x gives $1.39 \times 10^{-4} M$. 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: $[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4} M$ $[Fe(H_2O)_6{}^{2+}] = 0.120\, M$ $[OH^-] = 7.2 \times 10^{-11} M$

102. pH = 2.41
103. $[C_{10}H_{14}N_2] = 0.049\, M$ $[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4} M$ $[C_{10}H_{14}N_2H_2{}^{2+}] = 1.4 \times 10^{-11} M$ $[OH^-] = 1.9 \times 10^{-4} M$ $[H_3O^+] = 5.3 \times 10^{-11} M$
104. $K_a = 1.2 \times 10^{-2}$
105. $K_b = 1.77 \times 10^{-5}$
106. $0.014\, M$
107. $7.2 \times 10^{-15} M$
108. $4.4 \times 10^{-22} M$
109. $6.2 \times 10^{-6} M = [Hg^{2+}]$; $1.2 \times 10^{-5} M = [Cl^-]$; The substance is a weak electrolyte because very little of the initial 0.015 M $HgCl_2$ dissolved.
110. $[OH^-] = 4.5 \times 10^{-5}$; $[Al^{3+}] = 2.2 \times 10^{-20}$ (molar solubility)
111. $[SO_4{}^{2-}] = 0.049\ M$ $[Ba^{2+}] = 4.7 \times 10^{-7}$ (molar solubility)
112. $[OH^-] = 7.6 \times 10^{-3} M$ $[Pb^{2+}] = 2.1 \times 10^{-11}$ (molar solubility)
113. 7.66
114. $[CO_3{}^{2-}] = 0.116\ M$ $[Cd^{2+}] = 4.5 \times 10^{-11} M$
115. $3.1 \times 10^{-3} M$
116. 0.0102 L (10.2 mL)
117. 5.4×10^{-3} g
118. (a) $K_{sp} = [Mg^{2+}][F^-]^2 = (1.21 \times 10^{-3})(2 \times 1.21 \times 10^{-3})^2 = 7.09 \times 10^{-9}$; (b) $7.09 \times 10^{-7} M$ (c) Determine the concentration of Mg^{2+} and F^- that will be present in the final volume. Compare the value of the ion product $[Mg^{2+}][F^-]^2$ with K_{sp}. If this value is larger than K_{sp}, precipitation will occur. $0.1000\ L \times 3.00 \times 10^{-3} M\ Mg(NO_3)_2 = 0.3000\ L \times M\ Mg(NO_3)_2 M\ Mg(NO_3)_2 = 1.00 \times 10^{-3} M$ $0.2000\ L \times 2.00 \times 10^{-3} M\ NaF = 0.3000\ L \times M\ NaF\ M\ NaF = 1.33 \times 10^{-3} M$ ion product = $(1.00 \times 10^{-3})(1.33 \times 10^{-3})^2 = 1.77 \times 10^{-9}$ This value is smaller than K_{sp}, so no precipitation will occur. (d) MgF_2 is less soluble at 27 °C than at 18 °C. Because added heat acts like an added reagent, when it appears on the product side, the Le Châtelier's principle states that the equilibrium will shift to the reactants' side to counter the stress. Consequently, less reagent will dissolve. This situation is found in our case. Therefore, the reaction is exothermic.
119. BaF_2, $Ca_3(PO_4)_2$, ZnS; each is a salt of a weak acid, and the $[H_3O^+]$ from perchloric acid reduces the equilibrium concentration of the anion, thereby increasing the concentration of the cations
120. Effect on amount of solid $CaHPO_4$, $[Ca^{2+}]$, $[OH^-]$: (a) increase, increase, decrease; (b) decrease, increase, decrease; (c) no effect, no effect, no effect; (d) decrease, increase, decrease; (e) increase, no effect, no effect
121. 9.2 g