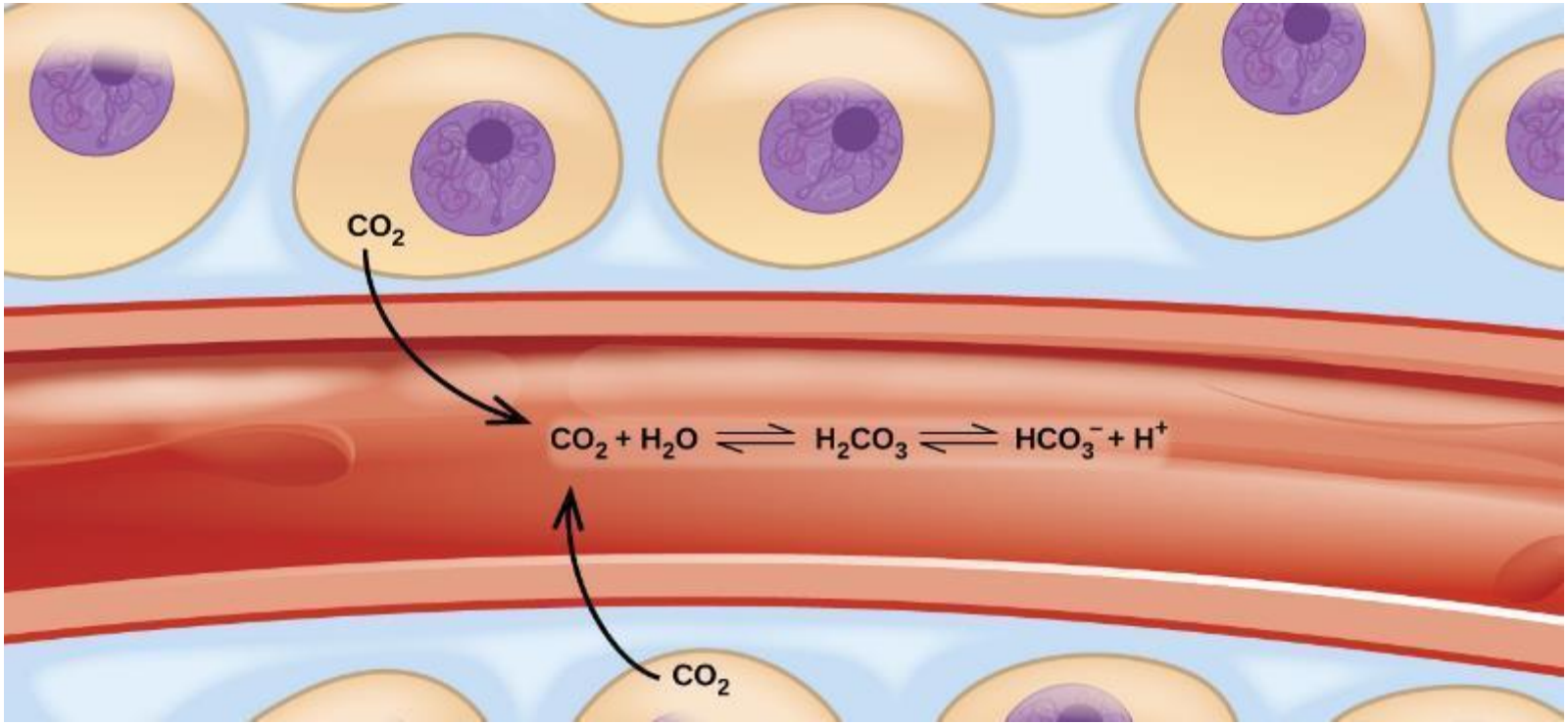
Unit 12 includes the following OpenStax sections

- 13.1 Chemical Equilibrium
- 13.2 Equilibrium Constants
- 13.3 Shifting Equilibria: Le Châtelier's Principle
- 13.4 Equilibrium Calculations
- 15.1 Precipitation and Dissolution

Figure 13.1



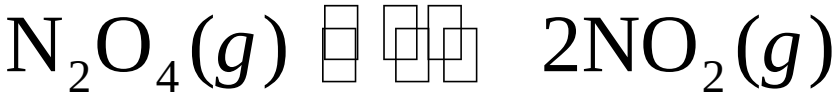
Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

Learning Objectives

- 13.1 Chemical Equilibria
  - Describe the nature of equilibrium systems
  - Explain the dynamic nature of a chemical equilibrium

- Reactions with an appreciable reverse reaction are often best represented as an **equilibrium**.

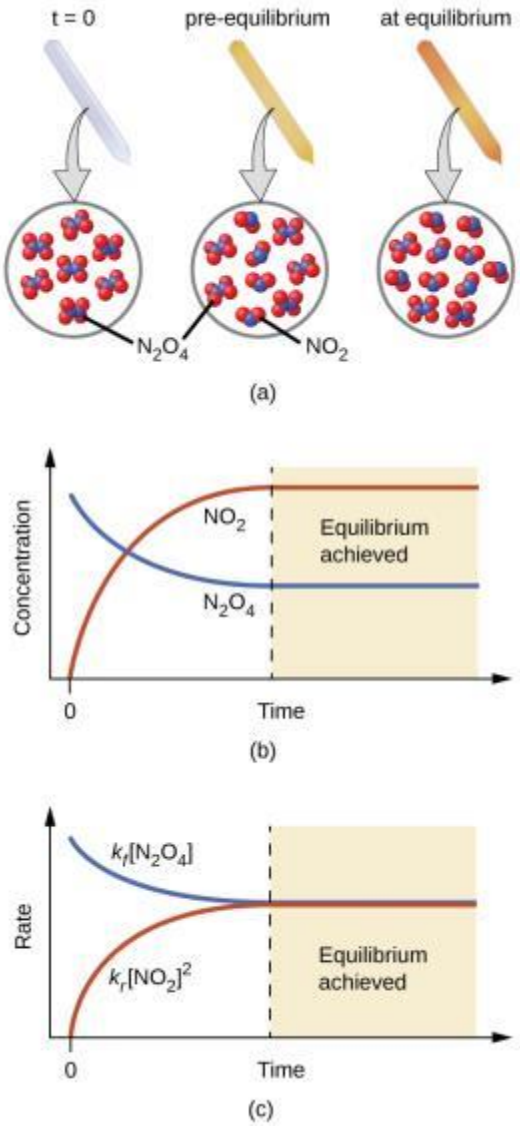
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



N_2O_4 is colorless. NO_2 is brown.

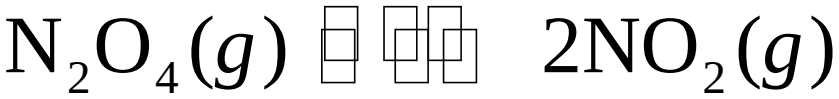
- When N_2O_4 is placed in a closed container at 100 °C, a reddish-brown color develops due to the formation of NO_2.
  - The forward reaction occurs.
- As NO_2 builds up, it can react to form N_2O_4
  - The reverse reaction occurs.
- At equilibrium, the amounts of reactants and products stop changing.

Figure 13.2



(a) A sealed tube containing colorless N2O4 darkens as it decomposes to yield brown NO2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

Establishment of Equilibrium



- The rate of the forward reaction starts out fast, but slows down as the concentration of N_2O_4 decreases.

- The rate of the reverse reaction starts out slow, but speeds up as the concentration of NO_2 increases.

- Once the rates of both reactions are equal, equilibrium is established.
  - No further changes in concentration of either gas occurs unless the temperature or the volume of the container is changed.

Common Equilibrium Misconceptions

1) The amount of reactants and products are ordinarily not equal to each other at equilibrium.

2) Although the amount of reactants and products remains constant at equilibrium, the system is not static at equilibrium.

Chemical equilibrium is a dynamic process.

Figure 13.3

A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

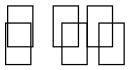
Figure 13.4

A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-ofelements.com/bromine.php)

Learning Objectives

- 13.2 Equilibrium Constants
  - 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

Equilibrium Constants

- The symbol  , placed between reactants and products, is used to designate reversible reactions.

- The **reaction quotient**, ***Q***, allows us to mathematically express the amounts of reactants and products present at any point in a reversible reaction.

The Reaction Quotient, Q

- Consider the general reaction:

$$mA + nB \rightleftharpoons xC + yD$$

  - A, B, C, D are either gases or aqueous species.
  - *m*, *n*, *x*, *y* are the coefficients in the balanced equation.

- When using amounts expressed in concentration, the reaction quotient is called *Qc*.

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

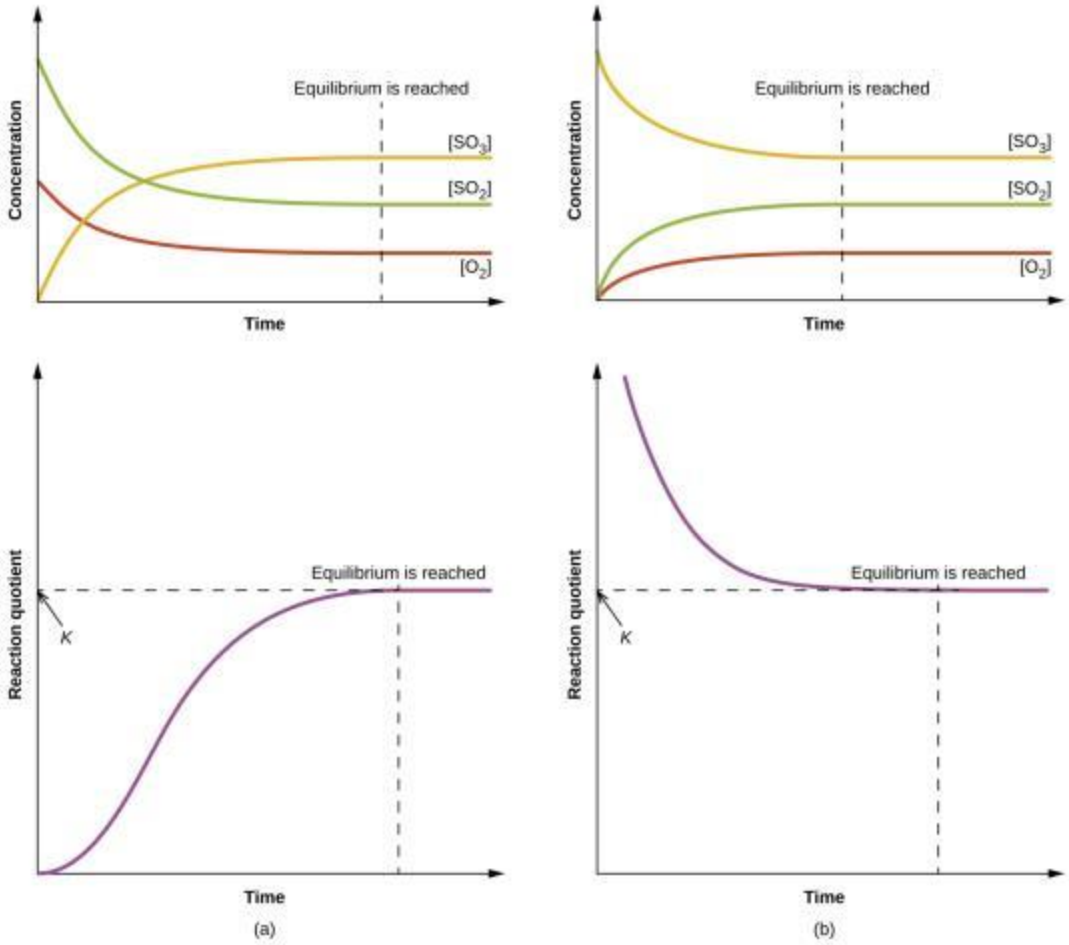
The Concentration Reaction Quotient, Q_c

- All concentrations must be expressed in **Molarity**.
- Product concentrations are in the numerator (multiplied together).
- Reactant concentrations are in the denominator (multiplied together).
- Each concentration is raised to the power of its coefficient from the **balanced** equation.

The Value of the Reaction Quotient, Q

- The numeric value of Q_c for a given reaction can vary prior to equilibrium.
- The value of Q_c depends on the concentration of products and reactants present at that particular moment.
- We can calculate Q_c at any point in a reaction.
- We will often calculate Q_c at the start of the reaction using initial concentrations.

Figure 13.5



Changes in concentrations and *Qc* for a chemical equilibrium achieved beginning with a (a) mixture of reactants only and (b) products only.

The Equilibrium Constant, K

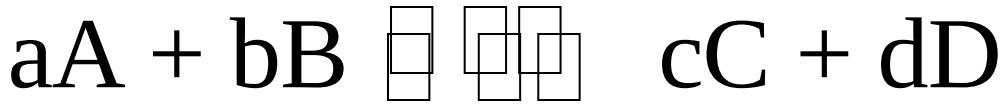
- The value of *Q* when the reaction is at equilibrium is called the **equilibrium constant (*K*)**.

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_C \text{ at equilibrium} = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Be careful not confuse with the kinetic rate constant (*k*).

Q and K



$$aA + bB \rightleftharpoons cC + dD$$

$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- The equilibrium constant (*K*) has the same form as the reaction quotient (*Q*).
  - For *K*, the concentrations *must* be those at equilibrium.
  - For *Q*, the concentrations can be those at any point in the reaction, *not necessarily* when at equilibrium.

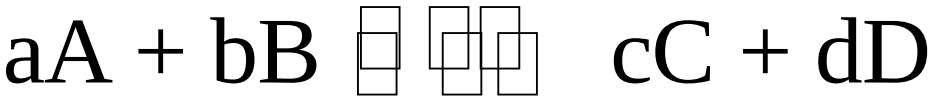
The Equilibrium Constant, K

- The value of the equilibrium constant is *independent* of the starting amounts of reactants and products.
- The value of the equilibrium constant is *dependent* on the temperature of the system.
- The magnitude of an equilibrium constant indicates the extent of a reaction.
- *K* and *Q* are unitless values.

The Magnitude of the Equilibrium Constant

- If *K* is very small, the mixture contains mostly reactants at equilibrium.
- If *K* is very large, the mixture contains mostly products at equilibrium.
- The value of *K* gives no indication as to whether the reaction is fast or slow.

Q, K, and the Direction of Reaction

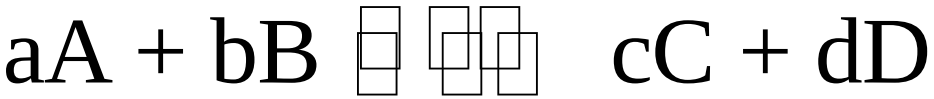


$$aA + bB \rightleftharpoons cC + dD$$

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

- A system that is not at equilibrium will proceed in the direction that establishes equilibrium.
- By comparing *Q* to *K*, it is possible to determine which direction the system will proceed to achieve equilibrium.

Q, K, and the Direction of Reaction



$$aA + bB \rightleftharpoons cC + dD$$

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

- When $Q < K$
- When $Q > K$
- When $Q = K$

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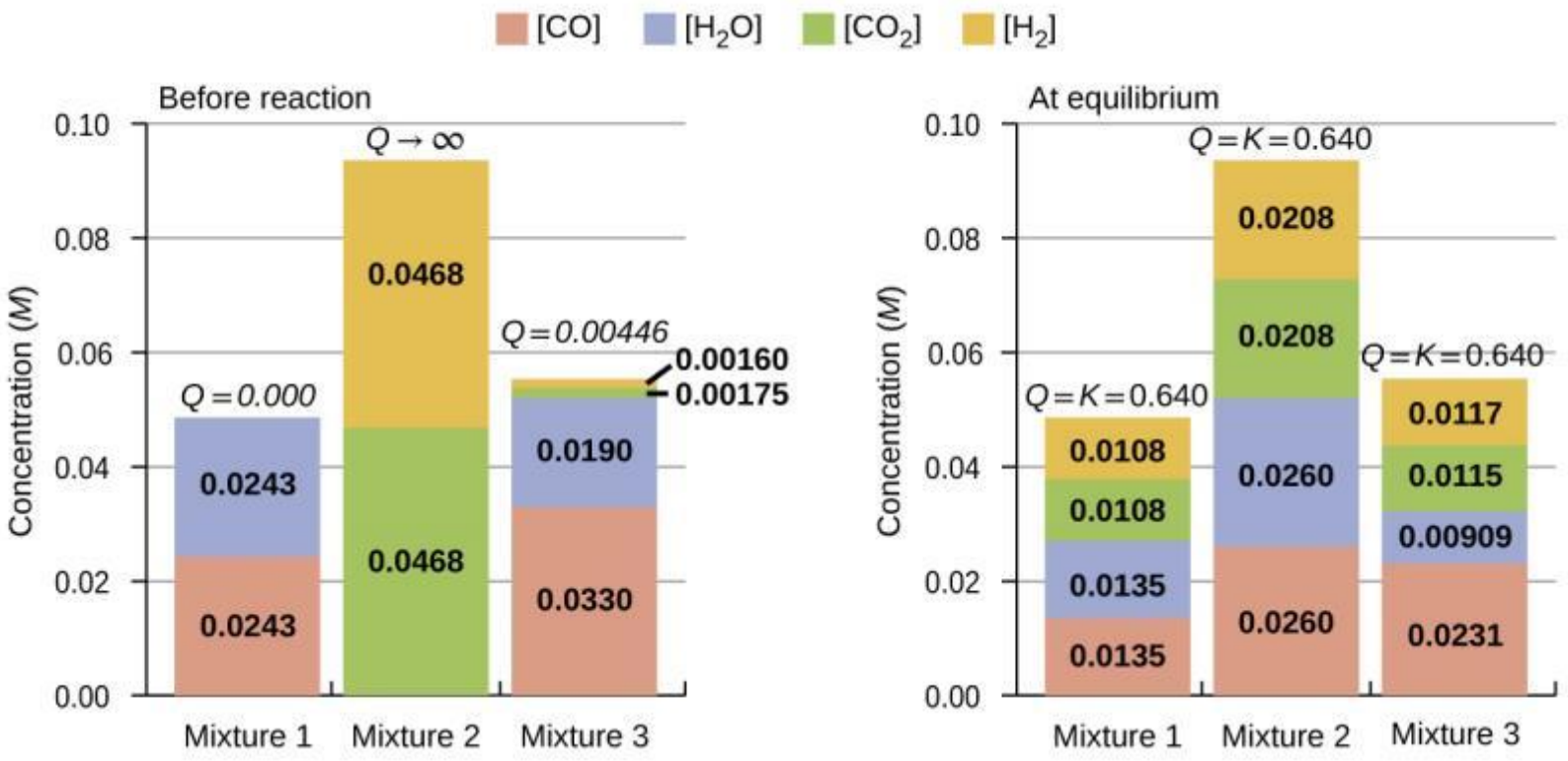
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

- There are many ways to approach the equilibrium state.

- Mixture 1: Start with just CO and H_2O.
- Mixture 2: Start with just CO_2 and H_2.
- Mixture 3: Start with CO, H_2O, CO_2, and H_2.

- The value of the equilibrium constant is *independent of the starting amounts* of the reactants and products.

Figure 13.6



Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$.

Homogenous Equilibrium

- A **homogenous equilibrium** is one in which all of the reactants and products are present in the same phase.
- Most commonly are either liquid or gaseous phases.
- Reaction quotients include concentration or pressure terms only for gaseous and solute species.
- For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products.

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$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq)$$

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

K_c and K_p

- For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products.

- A relation between these two *K* values may be simply derived from the ideal gas equation and the definition of molarity:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

$$= MRT$$

K_c and K_p

- The relationship between K_c and K_p:

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

- Δn is the change in the number of moles of gas.
- R = 0.08206 L · atm/mol · K
- T is temperature in Kelvin.

Heterogeneous Equilibrium

- Some reaction mixtures contain reactants and products that are in two or more different phases. These systems are called **heterogeneous equilibria**.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

- Pure solids and pure liquids *do not appear in the* K *expression*.

- The position of equilibrium is independent of the amount of solid or liquid present, *as long as at least some is present in the reaction mixture*.

Learning Objectives

- 13.3 Shifting Equilibria: Le Châtelier's Principle
  - Describe the ways in which an equilibrium system can be stressed
  - Predict the response of a stressed equilibrium using Le Chatelier's principle

Shifting Equilibria: Le Châtelier's Principle

Le Châtelier's Principle: *When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance.*

- At equilibrium $Q = K$.
- The disturbance causes a change in Q.
- The reaction will shift to re-establish $Q = K$.

Adding or Removing a Reactant or Product

- If a chemical equilibrium is disturbed by *adding* a reactant or product, the system will proceed in the direction that consumes *part* of the added species.

- If a chemical equilibrium is disturbed by *removing* a reactant or product, the system will proceed in the direction that restores *part* of the removed species.

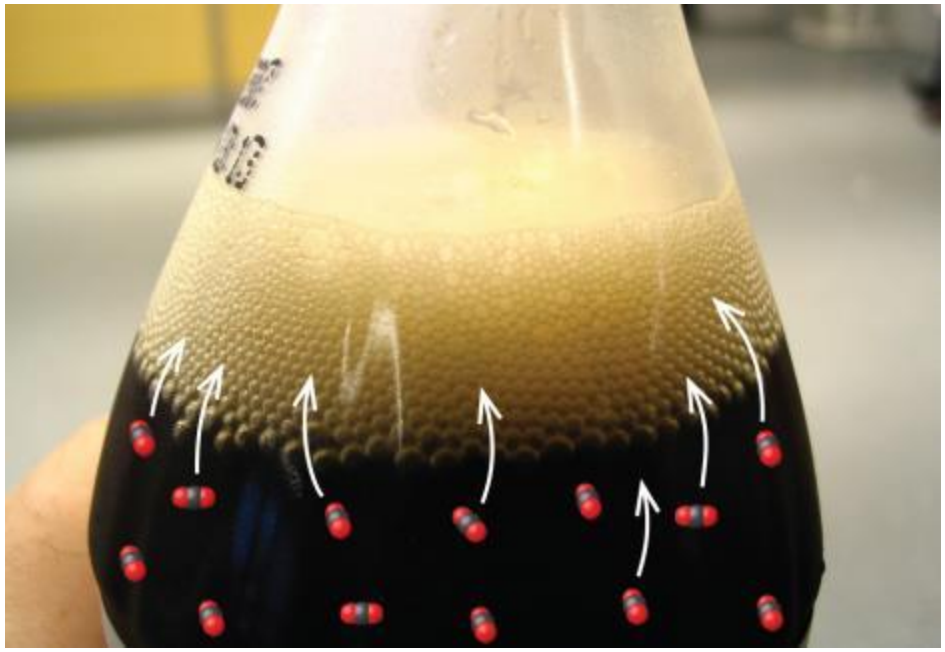
- The system responds in the way that restores equilibrium and therefore allows $Q = K$ again.

Adding or Removing a Pure Liquid or Solid

- Adding or removing a pure liquid or solid has *no effect* on the system unless all of the liquid or solid is removed.

- This is because pure liquids and solids do not appear in the equilibrium expression.

Figure 13.7



Changes in Temperature

- If you increase the temperature, you increase the heat. The equilibrium responds in a fashion that consumes the added heat.

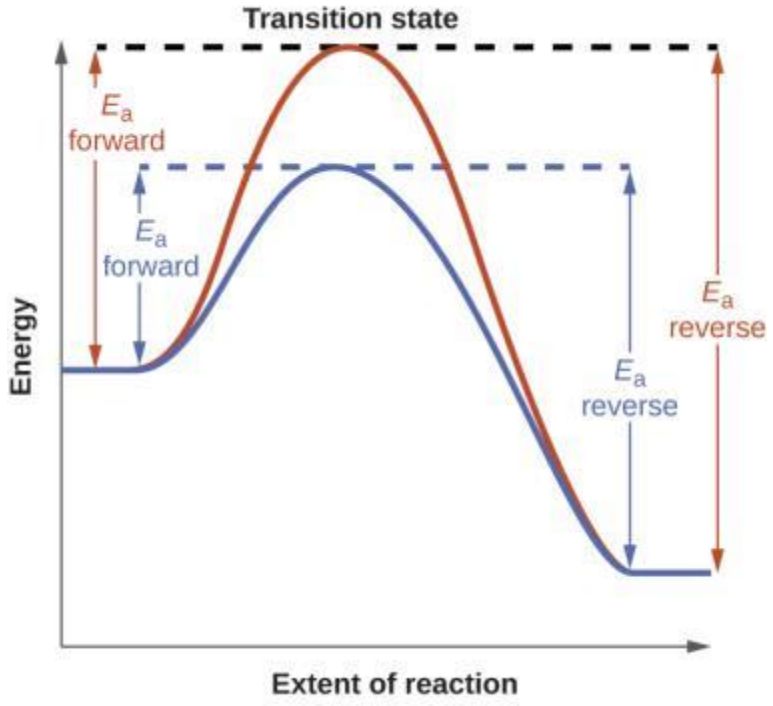
Temperature and the Equilibrium Constant

- Changing the temperature of a system results in a change in the value of the equilibrium constant.
- If the forward reaction is exothermic, then K decreases as T increases.
- If the forward reaction is endothermic, then K increases as T increases.

Catalysts do not Affect Equilibrium

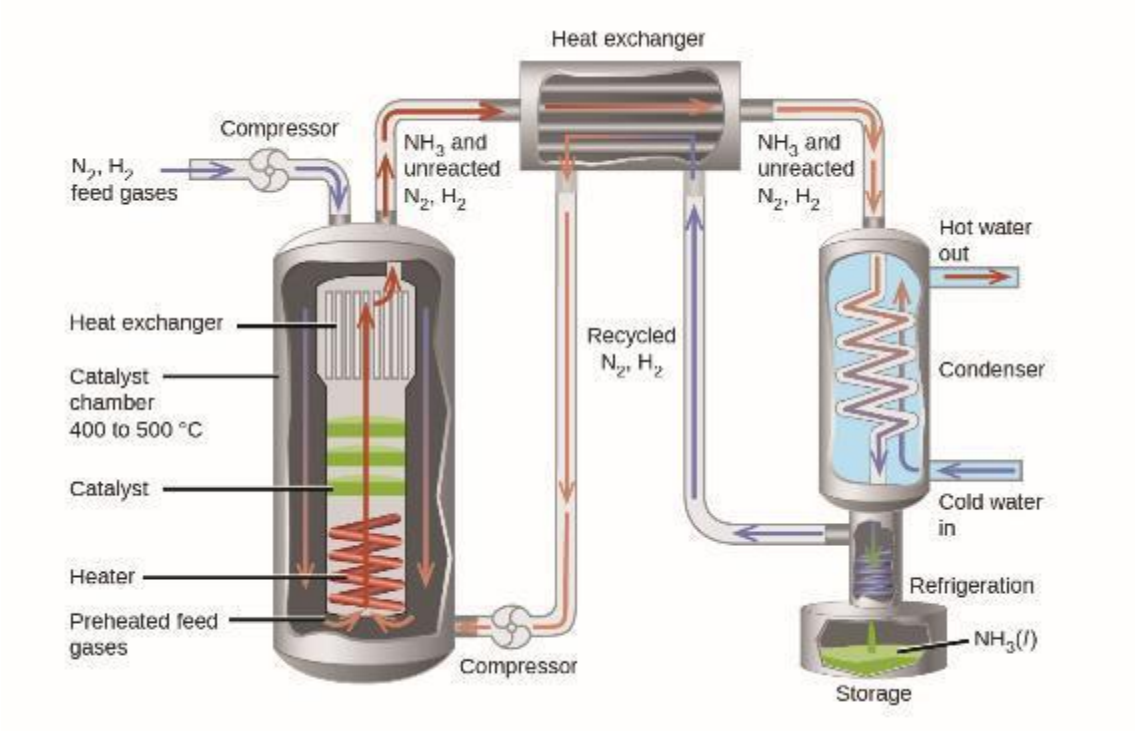
- A catalyst speeds up the rate of a reaction.
- For reversible reactions, catalysts increase the rates of the forward and reverse reactions.
- **Result**: A catalyst causes the system to reach equilibrium more quickly.
- But a catalyst does not affect the equilibrium concentrations or value of the equilibrium constant.

Figure 13.8



Reaction diagrams for an elementary process in the absence (red) and presence (blue) of a catalyst. The presence of catalyst lowers the activation energies of both the forward and reverse reactions but does not affect the value of the equilibrium constant.

Figure 13.9



The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favor product formation.

Learning Objectives

- 13.4 Equilibrium Calculations
  - Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
  - Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches

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Types of Equilibrium Calculations:

- Calculation of an equilibrium constant
- Calculation of missing equilibrium concentration or partial pressure
- Calculation of equilibrium concentrations (or partial pressures) from initial concentrations (or partial pressures)

Example 13.6

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

Example 13.6

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

Example 13.8

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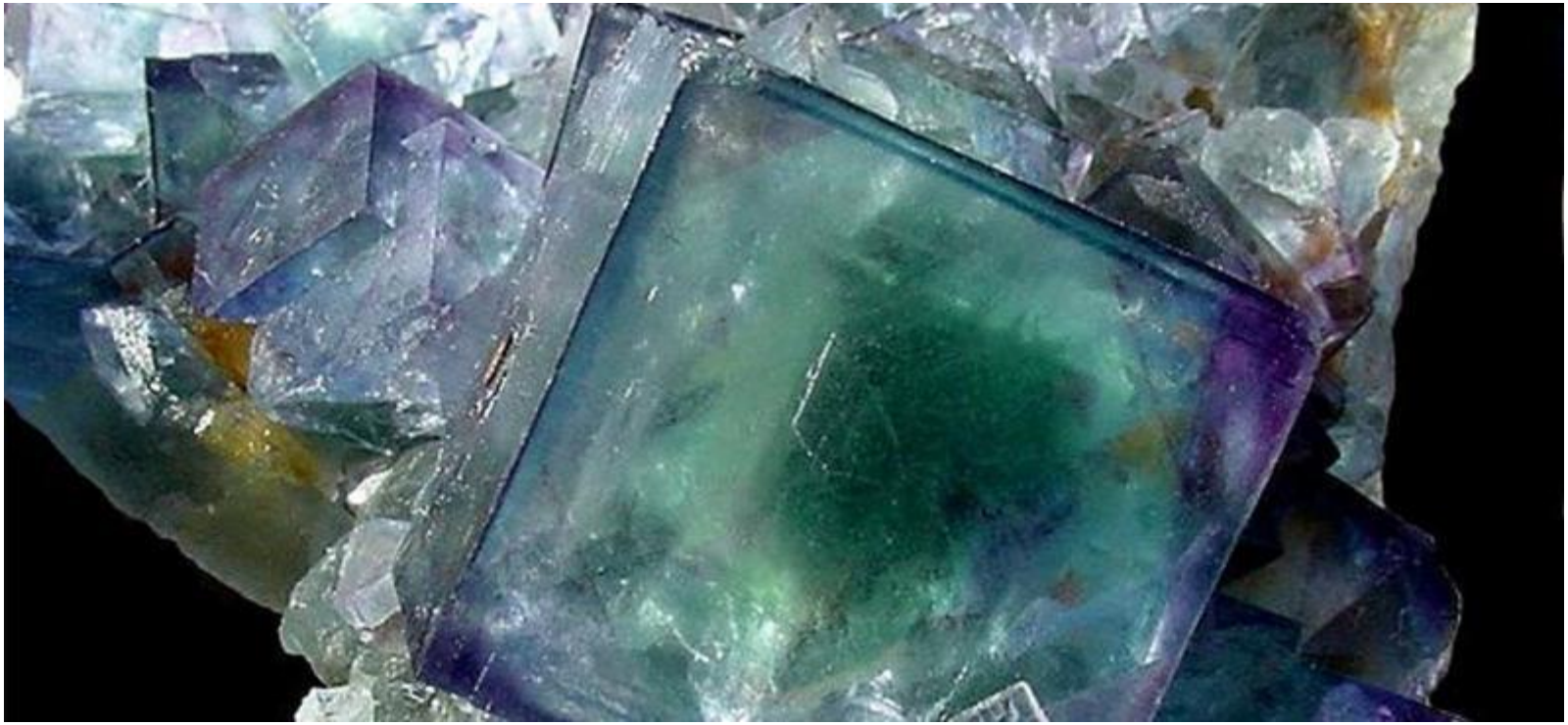
	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x	x

Example 13.9

openstax™

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

Figure 15.1



The mineral fluorite (CaF_2) is deposited through a precipitation process. Note that pure fluorite is colorless, and that the color in this sample is due to the presence of other metals in the crystal.

Learning Objectives

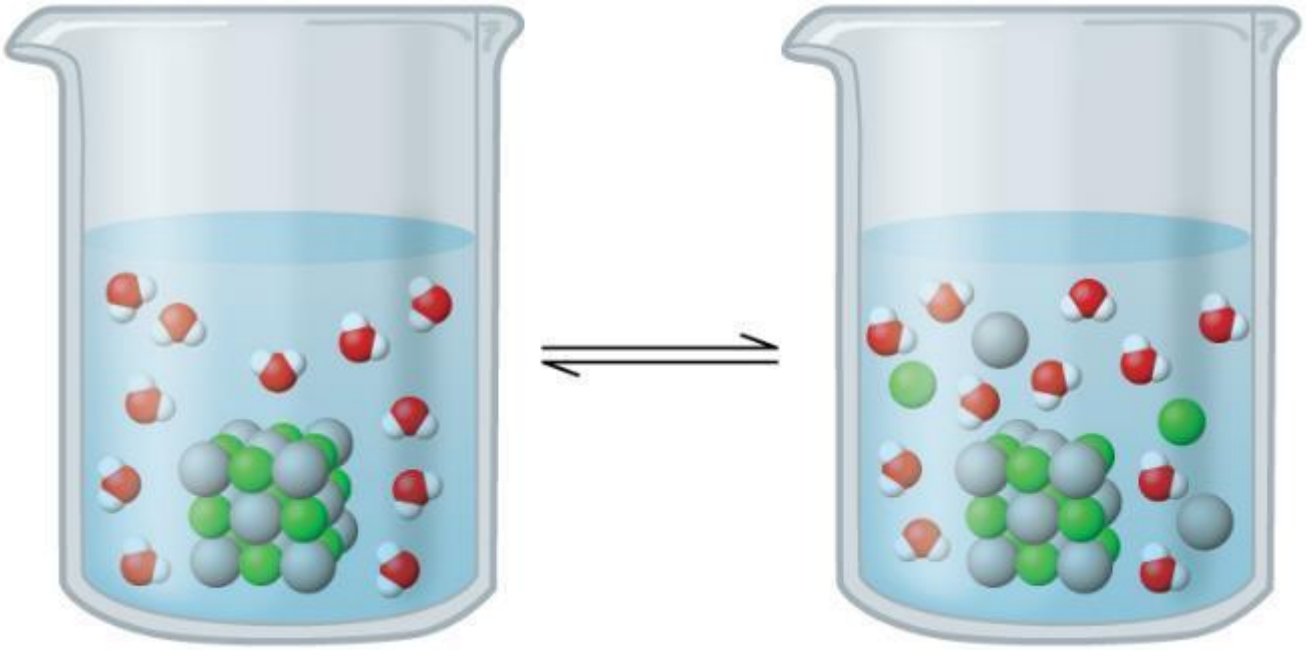
- 15.1 Precipitation and Dissolution
  - Write chemical equations and equilibrium expressions representing solubility equilibria
  - Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

Revisiting Solubility and Precipitation

- Previously you learned that some ionic compounds do not dissolve in water.
  - These are called **insoluble** compounds.
  - They do *b* dissociate into ions when placed in water.
  - Compounds that do dissolve by dissociating into their ions are called **soluble.**

- In reality, even insoluble compounds dissolve to a small extent. They are “sparingly soluble.”
  - An equilibrium exists between the precipitate and its ions.
  - Example: $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$ $K << 1$

Figure 15.2



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.

Solubility Product Constant, K_{sp}

- Consider the compound $SrCrO_4$

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

- K_{sp} is called the **solubility product constant**.
- At equilibrium, the solution is saturated with dissolved ions.

Interpreting the Solubility Expression and K_{sp}

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

$$K_{sp} = [Sr^{2+}][CrO_4^{2-}] = 3.6 \times 10^{-5} \text{ at } 25°$$

- Like all equilibrium constants, K_{sp} has a fixed value at a given temperature.

- The product of the two ion concentrations at equilibrium must have this value regardless of the direction from which equilibrium is approached.

K_{sp} and Water Solubility

- One way to establish a solubility equilibrium
  - Add a sparingly soluble solid to water and stir.
  - Eventually the solution becomes saturated with ions.
  - In other words, the compound reaches its solubility.
  - In a saturated solution, an equilibrium exists between the dissolved ions and undissolved solid.
  - We can calculate the solubility of a compound from its K_{sp} value.
  - The solubility will have units of moles per liter (*M*) and is called the **molar solubility**.

Calculating K_{sp} Given Solubility

- Instead of calculating solubility from K_{sp}, it is possible to calculate K_{sp} of a compound from its solubility.
  - There are many sources listing the solubility of sparingly soluble compounds.
  - Depending on the source, these solubility values are expressed in many different units.
  - We must always make sure that the solubility is the molar solubility (units of *M*) when using the K_{sp} expression.

K_{sp} and the Common Ion Effect

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

- How would you expect the solubility of barium sulfate in pure water to compare with its solubility in 0.10 M Na_2SO_4?
  - Solubility in 0.10 M Na_2SO_4 must be less than it is in pure water.
  - Recall Le Châtelier's Principle
    - The presence of the common ion, SO_4^{2-}, will drive the equilibrium to the left.
    - Common ions reduce solubility.

K_{sp} and the Common Ion Effect

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$$

- How would you expect the solubility of barium sulfate in pure water to compare with its solubility in 0.10 M NaCl?

Example 15.3

	$CuBr(s) \rightleftharpoons Cu^{+}(aq) + Br^{-}(aq)$		
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		x	x

Example 15.4

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

Figure 15.3

Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Example 15.6

	$Hg_2Cl_2\,(s) \rightleftharpoons Hg_2^{2+}\,(aq)$	+	$2Cl^-\,(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Figure 15.4

The suspension of barium sulfate coats the intestinal tract, which allows for greater visual detail than a traditional X-ray. (credit modification of work by “glitzy queen00”/Wikimedia Commons)

Solubility and Precipitates

- Recall, equilibrium can be approached from either direction.

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

- Starting with just reactants—Add solid compound to water.
- Starting with just products—Add ions to water.

Precipitate Formation

- Consider mixing two solutions:

$$Sr(NO_3)_2\ (aq) \text{ and } K_2CrO_4\ (aq)$$

K_{sp} and Precipitate Formation

- K_{sp} values can be used to predict whether a precipitate will form when ions (from solutions) are added to water.
  - Recall the use of Q, the reaction quotient.
  - Q is of the same form as K_{sp}, only difference is the concentrations at any particular moment can be used with Q and only equilibrium concentrations can be used with K_{sp}.

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

$$K_{sp} = [Sr^{2+}][CrO_4^{2-}] \qquad Q = [Sr^{2+}][CrO_4^{2-}]$$

K_{sp} and Precipitate Formation

$$K_{sp} = [Sr^{2+}][CrO_4^{2-}] \qquad Q = [Sr^{2+}][CrO_4^{2-}]$$

- The relative magnitude of Q vs. K_{sp} will indicate whether or not a precipitate will form.

$$SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq) + CrO_4^{2-}(aq)$$

- **If Q > K_{sp}, a precipitate will form**, decreasing the ion concentrations until equilibrium is established.

- **If Q < K_{sp}, the solution is unsaturated**, no precipitate will form, and if desired more compound can be dissolved.

- **If Q = K_{sp}, the solution is saturated**, just at the point of precipitation.

Selective Precipitation

- Consider a solution of two cations.
  - One way to separate the cations is to add an anion that will form a precipitate with only one of them.
  - The precipitate can then be removed by filtration.
  - The other cation will remain in the filtrate.
  - This approach is called **selective precipitation**, and is often used as a method of purification.

Selective Precipitation

- Example: Solution of magnesium and sodium ions.
  - Most sodium compounds are soluble in water.
  - Magnesium can form a compound with CO_3^{-2}, which is only sparingly soluble. K_{sp} $MgCO_3 = 6.8 \times 10^{-6}$

Selective Precipitation

- Now, consider a solution of magnesium and barium ions at the *same concentration*. CO_3^{2-} ions are slowly added.

- K_{sp} $BaCO_3 = 1.6 \times 10^{-9}$

- K_{sp} $MgCO_3 = \sim 1 \times 10^{-5}$

- The difference in solubility can still be used to separate the cations if CO_3^{2-} ions are added very carefully.

- Which carbonate complex will precipitate first?

  - We can't always just compare K_{sp} values to answer this question…

Selective Precipitation

- When can K_{sp} values alone be used to predict which compound will precipitate first?

1) Both ions to be separated must be at the same initial concentration.
2) Both complexes must have the same cation : anion ratio.

- Both of these criteria must be met. If not then calculations must be done to determine which compound will precipitate first.

Figure 15.5

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)

Figure 15.6

Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: “eutrophication&hypoxia”/WikimediaCommons)

Example 15.13

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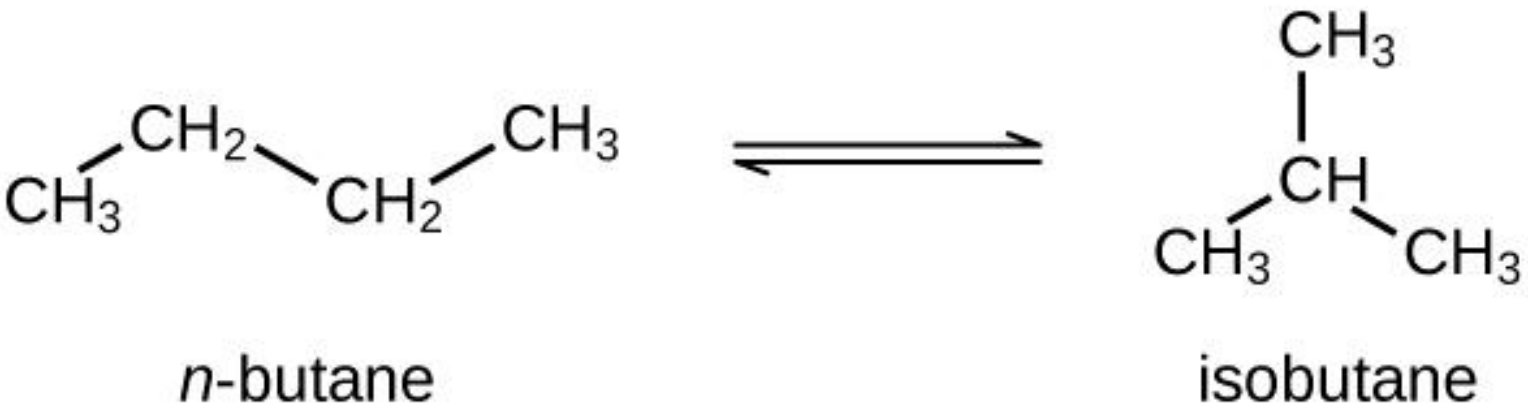
	$CdS\ (s) \rightleftharpoons Cd^{2+}\ (aq)$	+	$S^{2-}\ (aq)$
Initial concentration (*M*)		0.010	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		$0.010 + x$	x

Exercise 80



n-butane

isobutane

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