

Introductory Chemistry Fifth Edition Nivaldo J. Tro

Chapter 15

#### **Chemical Equilibrium**

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#### **Dynamic Equilibrium**

- Dynamic equilibrium involves two opposing processes occurring at the same rate.
- This image draws an analogy between a chemical equilibrium,

 $N_2O_4 \Longrightarrow 2NO_2$ 

in which the two opposing reactions occur at the same rate, and a freeway with traffic moving in opposing directions at the same rate.



**Equilibrium Involves Sameness and Constancy** 

- We can think of equilibrium as *sameness* and *constancy*.
- When an object is in equilibrium with its surroundings, some property of the object has reached sameness with the surroundings and is no longer changing.
- A cup of hot water is not in equilibrium with its surroundings with respect to temperature.
- If left undisturbed, the cup of hot water will slowly cool until it reaches equilibrium with its surroundings.
- At that point, the temperature of the water is the same as that of the surroundings (sameness) and no longer changes (constancy).

#### Life: Controlled Disequilibrium

- Part of a definition for living things is that living things are not in equilibrium with their surroundings.
- Our body temperature is not the same as the temperature of our surroundings.
- Living things, even the simplest ones, maintain some measure of *disequilibrium* with their environment.
- We add the concept of control to complete our definition of life with respect to equilibrium.

#### Life: Controlled Disequilibrium

- A cup of hot water is in disequilibrium with its environment, yet it is not alive.
- The cup of hot water has no control over its disequilibrium and will slowly come to equilibrium with its environment.
- In contrast, living things—as long as they are alive maintain and *control* their disequilibrium.
- Your body maintains your temperature within a specific range that is not in equilibrium with the surrounding temperature.
- So one definition for life is that living things are in *controlled disequilibrium* with their environment.
- A living thing comes into equilibrium with its surroundings only after it dies.

#### The Rate of a Chemical Reaction

- We examine the concept of equilibrium, especially chemical equilibrium—the state that involves sameness and constancy.
- Reaction rates are related to chemical equilibrium because a chemical system is at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.

#### **The Rate of a Chemical Reaction**

- The rate of a chemical reaction—a measure of how fast the reaction proceeds is defined as the amount of reactant that changes to product in a given period of time.
- In a reaction with a fast rate, the reactants react to form products in a short period of time.
- In a reaction with a slow rate, the reactants react to form products over a long period of time.
- Reaction rates can be controlled if we understand the factors that influence them.

#### **Collision Theory of Chemical Reactions**

- Chemical reactions occur through collisions between molecules or atoms.
- If the collision occurs with enough energy—that is, if the colliding molecules are moving fast enough—the reaction can proceed to form the products.
- If the collision occurs with insufficient energy, the reactant molecules bounce off one another without reacting.
- Since gas-phase molecules have a wide distribution of velocities, collisions occur with a wide distribution of energies.
- High-energy collisions lead to products; low-energy collisions do not.

#### **Collision Theory of Chemical Reactions**

- Higher-energy collisions are more likely to lead to products because most chemical reactions have an activation energy.
- Activation energy is an energy barrier that must be overcome for the reaction to proceed.
- The activation energy may be the energy required to begin to break the bonds of the reactants.
- If molecules react via high-energy collisions, then the factors that influence the rate of a reaction must be the same factors that affect the number of high-energy collisions that occur per unit time.
- The two most important factors are the *concentration* of the reacting molecules and the *temperature* of the reaction mixture.

#### How Concentration Affects the Rate of a Reaction

- The rate of a chemical reaction generally increases with increasing concentration of the reactants.
- The exact relationship between increases in concentration and increases in reaction rate varies for different reactions and is the subject of studies in chemical kinetics.



#### How Temperature Affects the Rate of a Reaction

- Raising the temperature makes the molecules move faster.
- More collisions occur per unit time, resulting in a faster reaction rate.
- A higher temperature results in more collisions that are of higher energy.
- Since it is the highenergy collisions that result in products, this also produces a faster rate.



### To summarize:

- Reaction rates generally increase with increasing reactant concentration.
- Reaction rates generally increase with increasing temperature.
- Reaction rates generally decrease as a reaction proceeds.

#### The Idea of Dynamic Chemical Equilibrium

- A reaction that can proceed in both the forward and reverse directions is a **reversible reaction**.
- In a chemical reaction, the condition in which the rate of the forward reaction equals the rate of the reverse reaction is called **dynamic equilibrium.**
- This condition is not static—it is dynamic because the forward and reverse reactions are still occurring but at the same constant rate.
- When dynamic equilibrium is reached, the concentrations of reactants and products no longer change.
- The reactants and products are being depleted at the same rate at which they are being formed.

#### Equilibrium

When the concentrations of the reactants and products no longer change, equilibrium has been reached.





#### Population Analogy for a Chemical Reaction Proceeding to Equilibrium

- Eventually, the rate of people moving out of Narnia (which has been slowing down as people leave) equals the rate of people moving back to Narnia (which has been increasing as Middle Earth gets more crowded).
- Dynamic equilibrium has been reached.



Equilibrium

#### The Equilibrium Constant K<sub>eq</sub>

A way to quantify the relative concentrations of the reactants and products at equilibrium

- When dynamic equilibrium is reached, the forward reaction rate is the same as the reverse reaction rate (sameness).
- Because the reaction rates are the same, the concentrations of the reactants and products no longer change (constancy).
- The constancy of concentrations of reactants and products at equilibrium does *not* imply that the concentrations of reactants and products are *equal* to one another at equilibrium.
- Some reactions reach equilibrium only after most of the reactants have formed products.
- Other reactions reach equilibrium when only a small fraction of the reactants have formed products.
- The amounts of reactants and products depend on the reaction and can be expressed numerically by the equilibrium constant  $K_{eq}$ .

#### The Equilibrium Constant K<sub>eq</sub>

• Consider the generic chemical reaction

 $aA + bB \Longrightarrow cC + dD$ 

where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the respective stoichiometric coefficients in the chemical equation.

 The equilibrium constant for the reaction is defined as the ratio—at equilibrium—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.



**Writing Equilibrium Expressions for Chemical Reactions** 

• Write an equilibrium expression for the reaction



 Notice that the *coefficients* in the chemical equation become the *exponents* in the equilibrium expression.

#### The Significance of the Equilibrium Constant

• *K*<sub>eq</sub> is large:

 $H_2(g) + Br_2(g) \implies 2 HBr(g)$   $K_{eq} = 1.9 \times 10^{19} \text{ at } 25 \text{ °C}$ 

•  $K_{eq}$  is small:

 $N_2(g) + O_2(g) \implies 2 \operatorname{NO}(g)$   $K_{eq} = 4.1 \times 10^{-31} \text{ at } 25 \,^{\circ}\text{C}$ 

The Meaning of a Large Equilibrium Constant

There will be a high concentration of *products* and a low concentration of reactants at equilibrium.

 $H_2(g) + Br_2(g) \implies 2 HBr(g)$ 



The Meaning of a Small Equilibrium Constant

There will be a high concentration of *reactants* and a low concentration of products at equilibrium.



What Does an Equilibrium Constant Imply about a Reaction?

#### To summarize:

- $K_{eq} << 1$  Reverse reaction is favored; forward reaction does not proceed very far.
- $K_{eq} \approx 1$  Neither direction is favored; forward reaction proceeds about halfway (significant amounts of both reactants and products are present at equilibrium).

K <sub>eq</sub>	>>	1
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1 Forward reaction is favored; forward reaction proceeds virtually to completion.

Heterogeneous Equilibria: The Equilibrium Expression for Reactions Involving a Solid or a Liquid

• The concentrations of pure solids and pure liquids are excluded from equilibrium expressions because they are constant.

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

 $K_{\rm eq} = [\rm CO_2]$ 

 Since CaCO<sub>3</sub>(s) and CaO(s) are both solids, they are omitted from the equilibrium expression.

#### **Calculating Equilibrium Constants**

$$H_2(g) + I_2(g) \Longrightarrow 2 HI(g)$$

- GIVEN:
   [H<sub>2</sub>] = 0.11 M
   [I<sub>2</sub>] = 0.11 M
   [HI] = 0.78 M
- FIND: K<sub>eq</sub>

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$
$$= \frac{[0.78]^2}{[0.11][0.11]}$$
$$= 5.0 \times 10^1$$

#### **Using Equilibrium Constants in Calculations**

 $2 \operatorname{COF}_2(g) \Longrightarrow \operatorname{CO}_2(g) + \operatorname{CF}_4(g) \qquad K_{eq} = 2.00 \text{ at } 1000 \,^{\circ}\mathrm{C}$ 

 GIVEN: [COF<sub>2</sub>] = 0.255 M [CF<sub>4</sub>] = 0.118 M *K*<sub>eq</sub> = 2.00
 FIND: [CO<sub>2</sub>]

$$K_{eq} = \frac{[CO_2][CF_4]}{[COF_2]^2}$$
$$CO_2] = K_{eq} \frac{[COF_2]^2}{[CF_4]}$$
$$CO_2] = 2.00 \frac{[0.255]^2}{[0.118]}$$
$$= 1.10 \text{ M}$$

#### Disturbing a Reaction at Equilibrium: Le Châtelier's Principle

• When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

#### **Population Analogy for Le Châtelier's Principle**

• When a system at equilibrium is disturbed, it shifts to minimize the disturbance. In this case, adding population to Middle Earth (the disturbance) causes population to move out of Middle Earth (minimizing the disturbance).



System responds

#### **Disturb a System by Adding Products**



 Figure 15.9 Le Châtelier's principle in action I: When a system at equilibrium is disturbed, it changes to minimize the disturbance: Adding NO<sub>2</sub> (the disturbance) causes the reaction to shift left, consuming NO<sub>2</sub> by forming more N<sub>2</sub>O<sub>4</sub>.

#### **Disturb a System by Adding Products**



**Disturb a System by Adding Reactants** 

 Figure 15.10 Le Châtelier's principle in action II: When a system at equilibrium is disturbed, it changes to minimize the disturbance: Adding N<sub>2</sub>O<sub>4</sub> (the disturbance) causes the reaction to shift right, consuming N<sub>2</sub>O<sub>4</sub> by producing more NO<sub>2</sub>.

#### **Disturb a System by Adding Reactants**



#### The Effect of a Volume Change on Equilibrium

- Changing the volume of a gas (or a gas mixture) results in a change in pressure.
- A *decrease* in volume causes an *increase* in pressure, and an *increase* in volume causes a *decrease* in pressure.
- From the ideal gas law, PV = nRT, we can see that lowering the number of moles of a gas (n) results in a lower pressure (P) at constant temperature and volume.
- A system can respond to a disturbance by changing the moles of gas present to relieve a pressure change.

#### **Effect of Volume Decrease on Equilibrium**

 When the volume of an equilibrium mixture decreases, the pressure increases. The system responds (to bring the pressure back down) by shifting to the right, the side of the reaction with the fewer moles of gas particles.



#### **Effect of Volume Increase on Equilibrium**

 When the volume of an equilibrium mixture increases, the pressure decreases. The system responds (to raise the pressure) by shifting to the left, the side of the reaction with more moles of gas particles.



#### The Effect of a Volume Change on Equilibrium

# To summarize, if a chemical system is at equilibrium, the effects of volume change are as follows:

- Decreasing the volume causes the reaction to shift in the direction that has fewer moles of gas particles.
- Increasing the volume causes the reaction to shift in the direction that has more moles of gas particles.
- Notice that if a chemical reaction has an equal number of moles of gas particles on both sides of the chemical equation, a change in volume has no effect.

Chemistry and Health: How a Developing Fetus Gets Oxygen from Its Mother

 Hemoglobin (Hb) reacts with oxygen according to the equilibrium equation:

 $Hb + O_2 \Longrightarrow HbO_2$ 

 The equilibrium constant for this reaction is neither large nor small. Consequently, the reaction shifts toward the right or the left depending on the concentration of oxygen.

#### Chemistry and Health: How a Developing Fetus Gets Oxygen from Its Mother

 As blood flows through the lungs, where oxygen concentrations are high, the equilibrium shifts to the right—hemoglobin loads oxygen.



 As blood flows through muscles and organs that are using oxygen (where oxygen concentrations have been depleted), the equilibrium shifts to the left hemoglobin unloads oxygen.

$$Hb + O_2 \iff HbO_2$$
Reaction shifts left

#### Chemistry and Health: How a Developing Fetus Gets Oxygen from Its Mother

 Fetal hemoglobin (HbF) is slightly different from adult hemoglobin. Like adult hemoglobin, fetal hemoglobin is in equilibrium with oxygen.

 $HbF + O_2 \Longrightarrow HbFO_2$ 

- The equilibrium constant for fetal hemoglobin is larger than the equilibrium constant for adult hemoglobin.
- Fetal hemoglobin will load oxygen at a lower oxygen concentration than adult hemoglobin.
- When the mother's hemoglobin flows through the placenta, it unloads oxygen into the placenta.
- Nature has engineered a chemical system in which the mother's hemoglobin can in effect hand off oxygen to the baby's hemoglobin.

The Effect of a Temperature Change on Equilibrium

- In an exothermic reaction, we can think of heat as a product. Raising the temperature of an exothermic reaction—think of this as adding heat to the product side—causes the reaction to shift left.
- In an *endothermic* reaction, we can think of heat as a reactant. Raising the temperature of an endothermic reaction—think of this as adding heat to the reactant side—causes the reaction to shift right.

### In an Exothermic Reaction, We Can Think of Heat as a Product

**Exothermic reaction:**  $A + B \Longrightarrow C + D + Heat$ 



## In an Endothermic Reaction, We Can Think of Heat as a Reactant

**Endothermic reaction:**  $A + B + Heat \implies C + D$ 





#### **Equilibrium as a Function of Temperature**

Since the reaction is endothermic, warm temperatures (a) cause a shift to the right, toward the production of brown NO<sub>2</sub>. Cool temperatures (b) cause a shift to the left, to colorless  $N_2O_4$ .





(a) Warm: NO<sub>2</sub>

**(b)** Cool: N<sub>2</sub>O<sub>4</sub>

#### To summarize:

- In an **exothermic** chemical reaction, heat is a product and the effects of temperature change are as follows:
- Increasing the temperature causes the reaction to shift left (in the direction of the reactants).
- Decreasing the temperature causes the reaction to shift right (in the direction of the products).
- In an *endothermic* chemical reaction, heat is a reactant and the effects of temperature change are as follows:
- Increasing the temperature causes the reaction to shift right (in the direction of the products).
- Decreasing the temperature causes the reaction to shift left (in the direction of the reactants).

#### **The Solubility-Product Constant**

- The process by which an ionic compound dissolves is an equilibrium process.
- The equilibrium expression for a chemical equation that represents the dissolving of an ionic compound is the solubility-product constant K<sub>sp</sub>.
- Solids are omitted from the equilibrium expression.
- A large K<sub>sp</sub> (forward reaction favored) means that the compound is very soluble. A small K<sub>sp</sub> (reverse reaction favored) means that the compound is not very soluble.

#### Writing Expressions for K<sub>sp</sub>

 To write the expression for *K*<sub>sp</sub>, first write the chemical reaction showing the solid compound in equilibrium with its dissolved aqueous ions. Then write the equilibrium expression based on this equation.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2 F^{-}(aq)$$
  
 $K_{sp} = [Ca^{2+}][F^{-}]^2$ 

## The *K*<sub>sp</sub> Value Is a Measure of the Solubility of a Compound

Compound	Formula	K <sub>sp</sub>
barium sulfate	$BaSO_4$	$1.07  imes 10^{-10}$
calcium carbonate	CaCO <sub>3</sub>	$4.96  imes 10^{-9}$
calcium fluoride	CaF <sub>2</sub>	$1.46  imes 10^{-10}$
calcium hydroxide	Ca(OH) <sub>2</sub>	$4.68  imes 10^{-6}$
calcium sulfate	$CaSO_4$	$7.10  imes 10^{-5}$
copper(II) sulfide	CuS	$1.27 \times 10^{-36}$
iron(II) carbonate	FeCO <sub>3</sub>	$3.07 \times 10^{-11}$
iron(II) hydroxide	Fe(OH) <sub>2</sub>	$4.87 imes10^{-17}$
lead(II) chloride	PbCl <sub>2</sub>	$1.17  imes 10^{-5}$
lead(II) sulfate	PbSO <sub>4</sub>	$1.82 \times 10^{-8}$
lead(II) sulfide	PbS	$9.04  imes 10^{-29}$
magnesium carbonate	MgCO <sub>3</sub>	$6.82  imes 10^{-6}$
magnesium hydroxide	Mg(OH) <sub>2</sub>	$2.06  imes 10^{-13}$
silver chloride	AgCl	$1.77  imes 10^{-10}$
silver chromate	Ag <sub>2</sub> CrO <sub>4</sub>	$1.12 \times 10^{-12}$
silver iodide	AgI	$8.51 \times 10^{-17}$

#### **TABLE 15.2** Selected Solubility-Product Constants (K<sub>sp</sub>)

#### Using K<sub>sp</sub> to Calculate Molar Solubility

Define the molar solubility

 (S) as Ba<sup>2+</sup>(aq) and
 SO<sub>4</sub><sup>2-</sup>(aq) molar
 concentrations at
 equilibrium.

• 
$$(S) = [Ba^{2+}] = [SO_4^{2-}]$$

$$K_{\rm sp} = [{\rm Ba}^{2^+}][{\rm SO}_4^{2^-}]$$
$$= S \times S$$
$$= S^2$$
Therefore
$$S = \sqrt{K_{\rm sp}}$$

$$S = \sqrt{K_{\rm sp}}$$
$$= \sqrt{1.07 \times 10^{-10}}$$
$$= 1.03 \times 10^{-5} \,\mathrm{M}$$

#### **Everyday Chemistry: Hard Water**

- Many areas of the United States obtain their water from lakes or reservoirs that have significant concentrations of CaCO<sub>3</sub> ( $K_{sp} =$ 4.96 × 10<sup>-9</sup>) and MgCO<sub>3</sub> ( $K_{sp} =$ 6.82 × 10<sup>-6</sup>).
- These salts dissolve into rainwater as it flows through soils rich in CaCO<sub>3</sub> and MgCO<sub>3</sub>.
- Water containing these salts is known as hard water.
- Hard water is not a health hazard because both calcium and magnesium are part of a healthy diet, but their presence in water can be annoying.



Hard water leaves scaly deposits on plumbing fixtures.

#### **Everyday Chemistry: Hard Water**

- Because of their relatively low solubility-product constants, water can easily become saturated with CaCO<sub>3</sub> and MgCO<sub>3</sub>.
- A drop of water becomes saturated with CaCO<sub>3</sub> and MgCO<sub>3</sub> as the water evaporates.
- A saturated solution such as this precipitates some of its dissolved ions.
- These precipitates show up as scaly deposits on faucets, sinks, and cookware. Washing cars or dishes with hard water leaves spots of CaCO<sub>3</sub> and MgCO<sub>3</sub> as these solids precipitate out of drying drops of water.

The Path of a Reaction and the Effect of a Catalyst

- The equilibrium constant describes how far a chemical reaction will go. The reaction rate describes how fast it will get there.
- The activation energy (or activation barrier) for a reaction is the energy barrier that must be overcome in order for the reactants to be converted into products.
- Activation energies exist for most chemical reactions because the original bonds must begin to break before new bonds begin to form, and this requires energy.

#### **How Activation Energies Affect Reaction Rates**



Reaction pathway

## Are There Any Ways to Speed Up a Slow Reaction (One with a High Activation Barrier)?

- For chemical reactions, the higher the activation energy, the fewer the number of reactant molecules that make it over the barrier, and the slower the reaction rate.
- In general: At a given temperature, the higher the activation energy for a chemical reaction, the slower the reaction rate.
- Are there any ways to speed up a slow reaction?
- Increase the concentrations of the reactants, which results in more collisions per unit time.
- Increase the temperature, which results in more collisions per unit time, and also in higher energy collisions.
- Use a *catalyst,* which lowers the activation energy barrier.

(a) One way to increase reaction rate is to push harder—this is analogous to an increase in temperature for a chemical reaction.
(b) Another way is to find a path that goes *around* the hill—this is analogous to the role of a catalyst for a chemical reaction.



#### **Function of a Catalyst**

A catalyst provides an alternate pathway with a lower activation energy barrier for the reaction.



#### Catalytic Destruction of Upper-Atmospheric Ozone

- Upper-atmospheric ozone forms a shield against harmful ultraviolet light that would otherwise enter Earth's atmosphere.
- Consider the noncatalytic destruction of ozone in the upper atmosphere.

 $O_3 + O \rightarrow 2 O_2$ 

- We have a protective ozone layer because this reaction has a fairly high activation barrier and therefore proceeds at a fairly slow rate. The ozone layer does not rapidly decompose into O<sub>2</sub>.
- However, the addition of CI (from synthetic chlorofluorocarbons) to the upper atmosphere has resulted in another pathway by which O<sub>3</sub> can be destroyed.
- The first step in this pathway—called the *catalytic* destruction of ozone—is the reaction

 $CI + O_3 \rightarrow CIO + O_2$ 

- In the case of the catalytic destruction of ozone, the catalyst speeds up a reaction that we do *not* want to happen.
- A catalyst does not change the *position* of equilibrium, only *how fast* equilibrium is reached.

#### **Enzymes: Biological Catalysts**

- Many reactants are thermally sensitive increasing the temperature often destroys them. The only way to carry out many reactions is to use catalysts.
- Most of the thousands of reactions that must occur for a living organism to survive would be too slow at normal temperatures. So living organisms use **enzymes**, biological catalysts that increase the rates of biochemical reactions.

#### FIGURE 15.17 An Enzyme Catalyst

The enzyme sucrase creates a pathway with a lower activation energy for the conversion of sucrose to glucose and fructose.



When Sucrose is in the Active Site, the bond between the glucose and fructose units weakens, lowering the activation energy for the reaction and increasing the reaction rate.



#### **Chapter 15 in Review**

- Equilibrium involves the ideas of sameness and constancy.
- The rate of a chemical reaction is the amount of reactant(s) that goes to product(s) in a given period of time.
- Dynamic chemical equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.
- In the equilibrium constant, K<sub>eq</sub>, only the concentrations of gaseous or aqueous reactants and products are included—the concentrations of solid or liquid reactants or products are omitted.

#### **Chapter 15 in Review**

- Le Châtelier's principle states that when a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.
- The solubility-product constant,  $K_{sp}$ , describes the dissolving of an ionic compound.
- Most chemical reactions must overcome an activation energy. A catalyst—a substance that increases the rate of the reaction but is not consumed by it—lowers the activation energy.

#### **Chemical Skills Learning Objectives**

- 1. LO: Write equilibrium expressions for chemical reactions.
- 2. LO: Calculate equilibrium constants.
- 3. LO: Use the equilibrium constant to find the concentration of a reactant or product at equilibrium.
- 4. LO: Restate and apply Le Châtelier's principle.
- 5. LO: Write an expression for the solubilityproduct constant.
- 6. LO: Use  $K_{sp}$  to determine molar solubility.