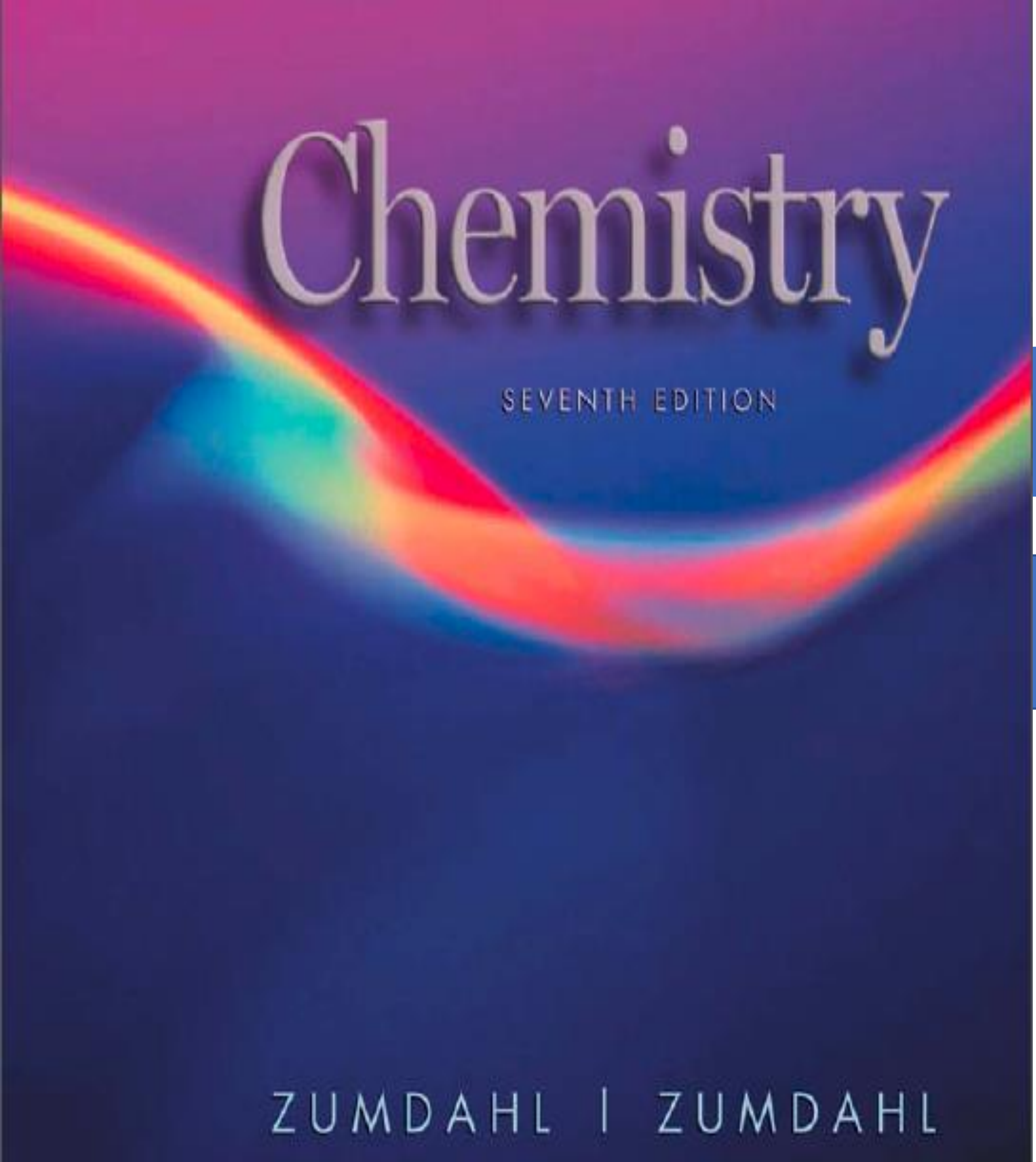


Chapter 7

Chemical equilibrium

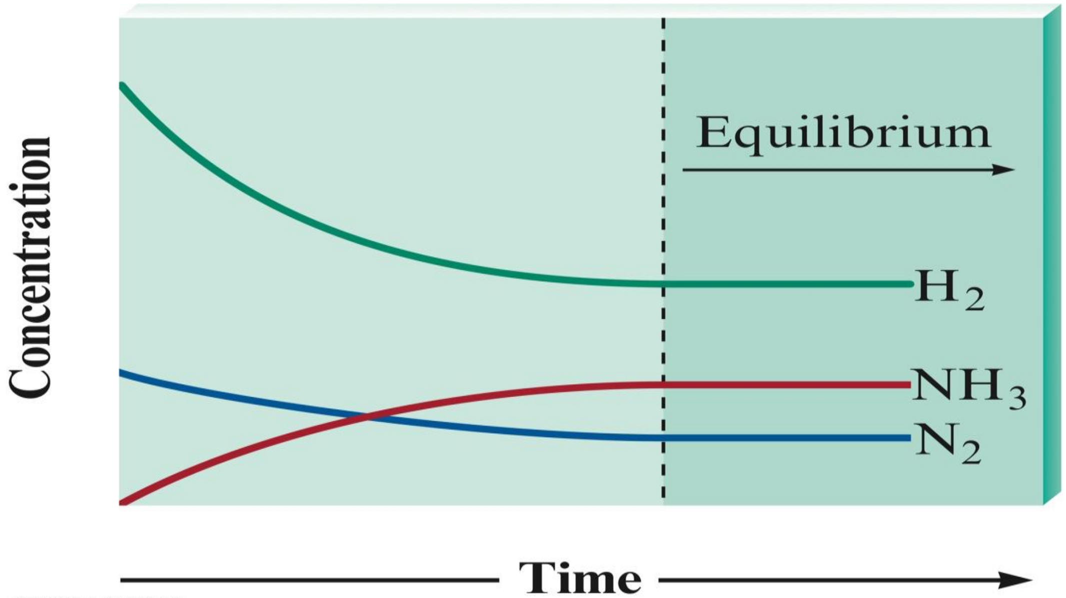
- The Characteristics of Chemical Equilibrium

❑ Chemical equilibrium is the state where the concentrations of all reactants and products remain constant with time

❑ There are two possible reasons why the concentrations of the reactants and products of a given chemical reaction remain unchanged when mixed.

1. The system is at chemical equilibrium.
2. The forward and reverse reactions are so slow that the system moves toward equilibrium at a rate that cannot be detected.

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



- The Equilibrium Constant
- The law of mass action postulated that for a reaction of the type:

$$jA + kB \rightleftharpoons lC + mD$$

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

  - A, B, C, and D = chemical species.
  - Square brackets = concentrations of species at equilibrium.
  - *j, k, l,* and *m* = coefficients in the balanced equation.
  - *K* = equilibrium constant (given without units).

Sample Exercise 7.1

- Write the equilibrium expression for the following reaction:

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$$

- ***Solution***
- Applying the law of mass action gives

Coefficient of NO_2

Coefficient of H_2O

$$K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

Coefficient of O_2

Coefficient of NH_3

Sample Exercise 7.2

- The following equilibrium concentrations were observed for the Haber process at 127^0C

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

$$[NH_3] = 3.1 \times 10^{-2} \text{ mol/L}$$
$$[N_2] = 8.5 \times 10^{-1} \text{ mol/L}$$
$$[H_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

- Calculate the value of K at 127^0C for this reaction.
- ***Solution***
- The balanced equation for the Haber process is

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

- thus

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

• Equilibrium Expressions Involving Pressures

- The relationship between the pressure and the concentration of a gas can be seen from the ideal gas equation:

$$PV = nRT \qquad \text{or} \qquad P = \left(\frac{n}{V}\right)RT = CRT$$

- For the ammonia synthesis reaction, the equilibrium expression can be written in terms of concentrations, that is,

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

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}{}^2}{(C_{N_2})(C_{H_2}{}^3)} = K_c$$

- or in terms of the *equilibrium partial pressures of the gases,* that is,

$$K_p = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}$$

K involves concentrations.

Kp involves pressures.

Sample Exercise 7.3

- The reaction for the formation of nitrosyl chloride

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

- was studied at 25^{0}C.The pressures at equilibrium were found to be
- $P_{NOCl} = 1.2$ atm , $P_{NO} = 5.0 \times 10^{-2}$ atm , and $P_{Cl_2} = 3.0 \times 10^{-1}$ atm
- Calculate the value of *Kp*for this reaction at 25^{0}C.
- ***Solution***
- *For this reaction*

$$K_p = \frac{{P_{NOCl}}^2}{(P_{NO_2})^2(P_{Cl_2})} = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2(3.0 \times 10^{-1})}$$

$$= 1.9 \times 10^3$$

- The Relationship Between K and K_p

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

- Δn = sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.
- R = 0.08206 L·atm/mol·K
- T = temperature (in Kelvin)

Sample Exercise 7.4

- Using the value of *Kp*obtained in Sample Exercise 7.3, calculate the value of *K* at for the reaction

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

- ***Solution***
- From the value of *Kp*, we can calculate *K* using

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

where $T = 25 + 273 = 298$ K and

$$\Delta n = \underbrace{2}_{\text{Sum of product coefficients}} - \underbrace{(2 + 1)}_{\text{Sum of reactant coefficients}} = -1$$

- Thus

$$K_p = K(RT)^{-1} = \frac{K}{RT}$$

$$K = K_p(RT) = (1.9 \times 10^3)(0.08206)(298) = 4.6 \times 10^4$$

Homogeneous Equilibria

- Homogeneous equilibria – involve the same phase:

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

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

Heterogeneous Equilibria

- Heterogeneous equilibria – involve more than one phase:

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

- The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.
  - The concentrations of pure liquids and solids are constant

- Thus the equilibrium constant will be

$$K = [CO_2]$$

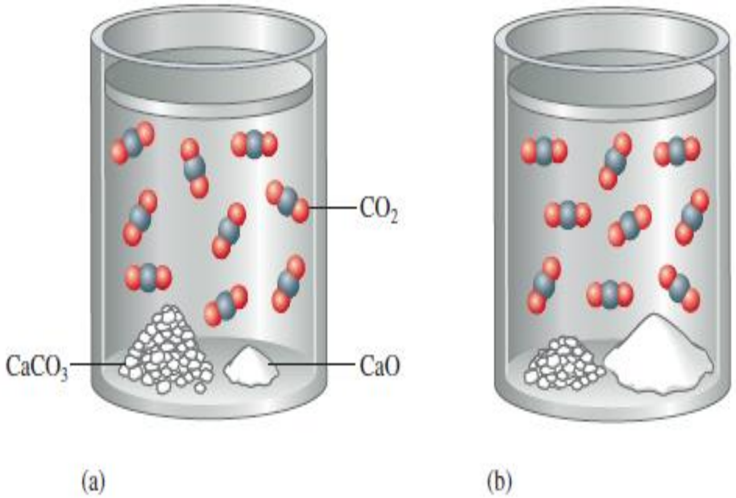


FIGURE 13.6
The position of the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ does not depend on the amounts of $CaCO_3(s)$ and $CaO(s)$ present.

- For example, in the decomposition of liquid water to gaseous hydrogen and oxygen

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

- where

$$K = [H_2]^2[O_2] \quad \text{and} \quad K_p = (P_{H_2}{}^2)(P_{O_2})$$

- if the reaction were carried out under conditions where the water is a gas rather than a liquid, that is,

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

- Then

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2} \quad \text{and} \quad K_p = \frac{(P_{H_2}{}^2)(P_{O_2})}{P_{H_2O}{}^2}$$

Sample Exercise 7.5

- Write the expressions for *K* and *Kp* for the following processes:

  a. Solid phosphorus pentachloride decomposes to liquid phosphorus trichloride and chlorine gas.

  b. Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.

- ***Solution***
- **a.** The reaction is

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

- The equilibrium expressions are

$$K = [Cl_2] \qquad \text{and} \qquad K_p = P_{Cl_2}$$

- **b.** The reaction is

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$$

- The equilibrium expressions are

$$K = [H_2O]^5 \qquad \text{and} \qquad K_p = (P_{H_2O})^5$$

- The Extent of a Reaction
  - A value of *K* much larger than 1 means that at equilibrium the reaction system will consist of mostly products – the equilibrium lies to the *right*.
    - Reaction goes essentially to completion
  - A very small value of *K* means that the system at equilibrium will consist of mostly reactants – the equilibrium position is far to the *left*.
    - Reaction does not occur to any significant extent
- Reaction Quotient, Q
  - Used when all of the initial concentrations are nonzero.
  - Apply the law of mass action using initial concentrations instead of equilibrium concentrations.
- For example

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

$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}}$$

- Where the subscript zeros indicate initial concentrations.

- *If $Q = K$*; The system is at equilibrium. No shift will occur.
- *Q is greater than K ($Q > K$)*; The system shifts to the left.
  - Consuming products and forming reactants, until equilibrium is achieved.
- *Q is less than K ($Q < K$)*; The system shifts to the right.
  - Consuming reactants and forming products, to attain equilibrium.

Sample Exercise 7.5

- For the synthesis of ammonia at 500^0Cthe equilibrium constant is $6x10^{-2}$. Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

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

a. $[NH_3]_0 = 1.0 \times 10^{-3}\ M$; $[N_2]_0 = 1.0 \times 10^{-5}\ M$; $[H_2]_0 = 2.0 \times 10^{-3}\ M$
b. $[NH_3]_0 = 2.00 \times 10^{-4}\ M$; $[N_2]_0 = 1.50 \times 10^{-5}\ M$; $[H_2]_0 = 3.54 \times 10^{-1}\ M$
c. $[NH_3]_0 = 1.0 \times 10^{-4}\ M$; $[N_2]_0 = 5.0\ M$; $[H_2]_0 = 1.0 \times 10^{-2}\ M$

- ***Solution***
- **a.** First we calculate the value of *Q*:

$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3}$$
$$= 1.3 \times 10^7$$

- Since $K = 6x10^{-2}$, *Q* is much greater than *K*. To attain equilibrium The system will shift to the left

$$N_2 + 3H_2 \longleftarrow 2NH_3$$

- **b.** We calculate the value of *Q*:

$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3} = \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.54 \times 10^{-1})^3} = 6.01 \times 10^{-2}$$

- In this case Q=K, so the system is at equilibrium. No shift will occur.
- In the same manner we can calculate the third required.

- Le Châtelier's Principle
- If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

- Effects of Changes on the System

1-Concentration: If a component (reactant or product) is added to a reaction system at equilibrium (at constant T and P or constant T and V), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.

2-Pressure:

a) The system will shift away from the added gaseous component. If a component is removed, the opposite effect occurs.

b) The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.

c) When the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume.

3-Temperature:

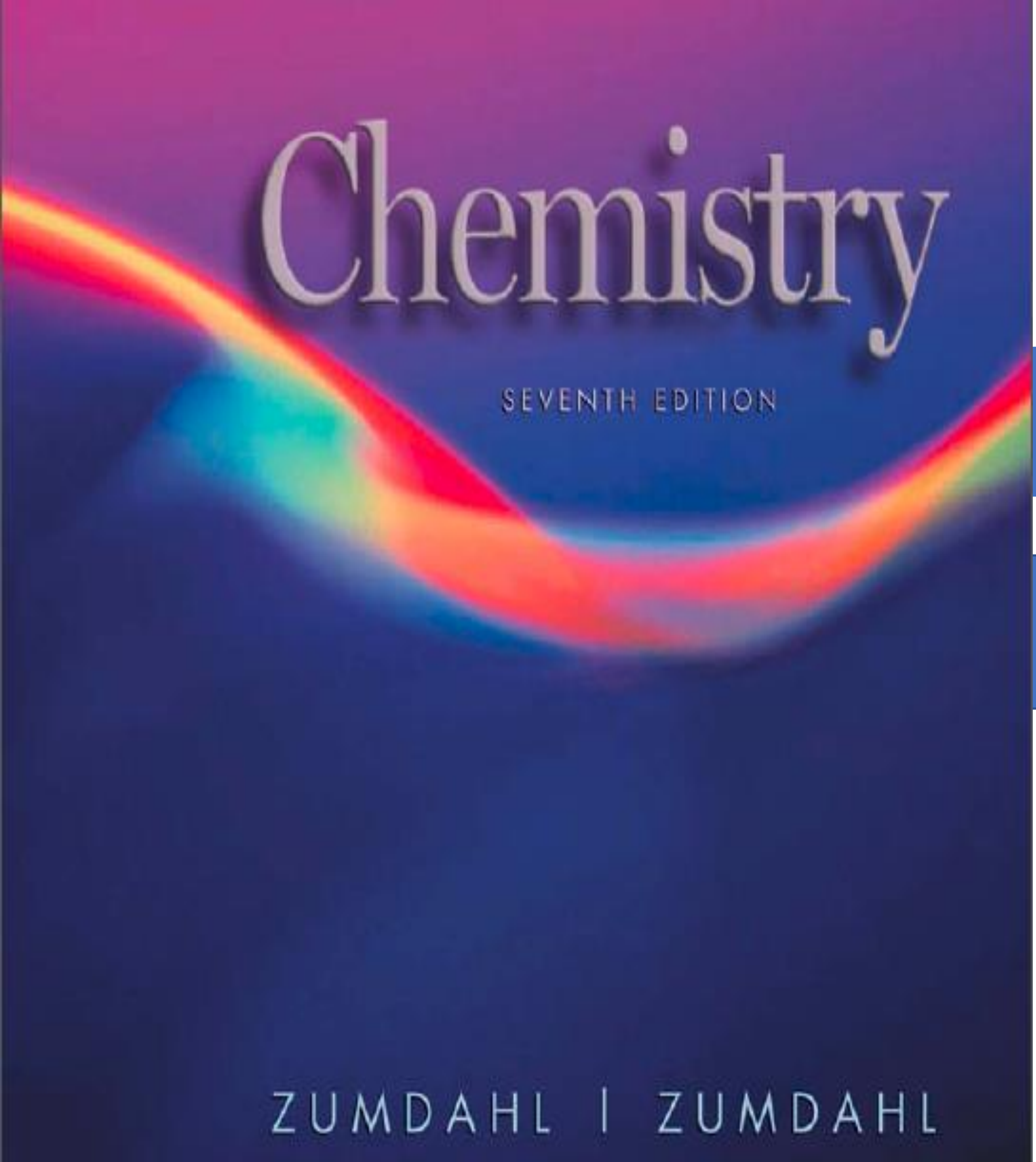
K will change depending upon the temperature (endothermic – energy is a reactant; exothermic – energy is a product).

Sample Exercise 7.6

- For each of the following reactions, predict how the value of *K* changes as the temperature is increased.

a. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\qquad \Delta H° = 181\ \text{kJ}$
b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\qquad \Delta H° = -198\ \text{kJ}$

- ***Solution***
- a. This is an endothermic reaction (*ΔH^0 is positive*), so that the *K* increases (the equilibrium shifts to the right) as the temperature is increased.
- b. This is an exothermic reaction (*ΔH^0 is negative*), so that the *K* decreases (the equilibrium shifts to the left) as the temperature is increased



Chapter 8

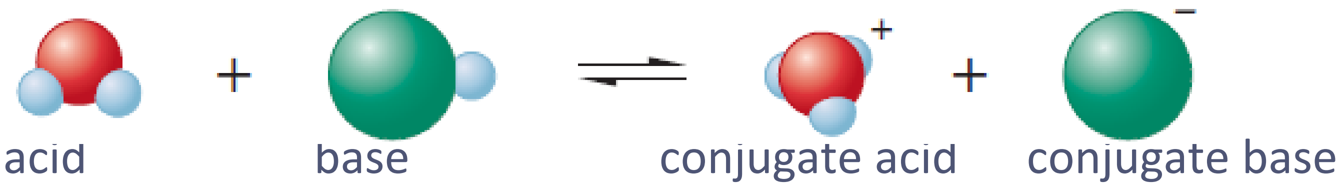
Acids and Bases

- Models of Acids and Bases
  - Arrhenius: Acids produce H^+ ions in solution, bases produce OH^- ions.
  - Brønsted–Lowry: Acids are proton (H^+) donors, bases are proton acceptors.

$$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$$

Acid in Water

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$



- Conjugate base is everything that remains of the acid molecule after a proton is lost.
- Conjugate acid is formed when the proton is transferred to the base.

- Acid Ionization Equilibrium
- The equilibrium expression for the reaction given in Equation

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}$$

- where *Ka* is called the **acid dissociation constant**

Sample Exercise 8.1

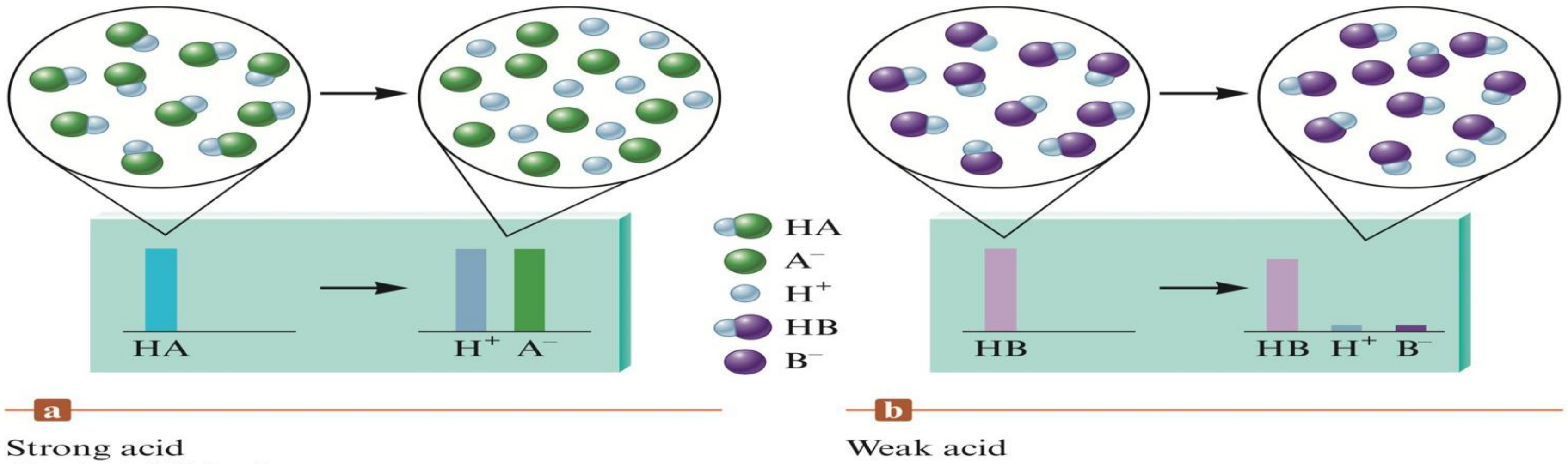
- Write the simple dissociation (ionization) reaction (omitting water) for each of the following acids.

a. Hydrochloric acid (HCl)
b. Acetic acid ($HC_2H_3O_2$)
c. The ammonium ion (NH_4^+)
d. The anilinium ion ($C_6H_5NH_3^+$)
e. The hydrated aluminum(III) ion $[Al(H_2O)_6]^{3+}$

- ***Solution***

a. $HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$
b. $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$
c. $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$
d. $C_6H_5NH_3^+(aq) \rightleftharpoons H^+(aq) + C_6H_5NH_2(aq)$
e. $Al(H_2O)_6^{3+}(aq) \rightleftharpoons H^+(aq) + Al(H_2O)_5OH^{2+}(aq)$

- Acid Strength
- Strong acid:
  - Ionization equilibrium lies far to the right.
  - Yields a weak conjugate base.
- Weak acid:
  - Ionization equilibrium lies far to the left.
  - Weaker the acid, stronger its conjugate base.



- Sulfuric acid is actually a **diprotic acid**, an acid having two acidic protons. The acid H_2SO_4 is a strong acid, virtually100% dissociated (ionized) in water:

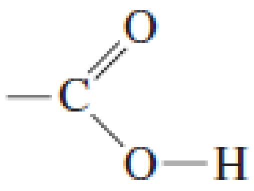
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

- The ion HSO_4^-, however, is a weak acid:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

- **Oxyacids**, in which the acidic proton is attached to an oxygen atom. such as phosphoric acid (H_3PO_4), nitrous acid (HNO_2), and hypochlorous acid (HOCl)

- **Organic acids**, those with a carbon atom backbone, commonly contain the **carboxyl group:**



- Examples: acetic acid (CH_3COOH-$HC_2H_3O_2$), and benzoic acid (C_6H_5COOH).

- Water as an Acid and a Base
  - Water is amphoteric:
    - Behaves either as an acid or as a base.
    - Auto-Ionization of Water

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

- leads to the equilibrium expression

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

- where Kw, called the ion-product constant (or the dissociation constant for water).
- At 25^{0}C in pure water

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\,M$$

- This means that at 25^{0}C

$$K_w = [H^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- At 25° C:

  $$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- *No matter what the solution contains*, the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14} at 25° C.

- Three Possible Situations

- $[H^+] = [OH^-]$; *neutral* solution
- $[H^+] > [OH^-]$; *acidic* solution
- $[OH^-] > [H^+]$; *basic* solution

Section 8.2

acid strength

Sample Exercise 8.2

- Calculate $[H^+]$ and $[OH^-]$or as required for each of the following solutions at 25^0C , and state whether the solution is neutral, acidic, or basic.

  a. $1.0 \times 10^{-5}\ M\ OH^-$
  b. $1.0 \times 10^{-7}\ M\ OH^-$
  c. $10.0\ M\ H^+$

- ***Solution***

  a. $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$. Since $[OH^-]$ is $1.0 \times 10^{-5}\ M$, solving for $[H^+]$ gives

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9}\ M$$

  Since $[OH^-] > [H^+]$, the solution is basic.

- b. solving (b) in the same manner as solving (a).

  c. Solving for $[OH^-]$ gives

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{10.0} = 1.0 \times 10^{-15}\ M$$

  Since $[H^+] > [OH^-]$, the solution is acidic.

Section 8.3
The pH Scale

- The pH is a log scale based on 10, where pH = –log[H$^+$]
- Thus for a solution where

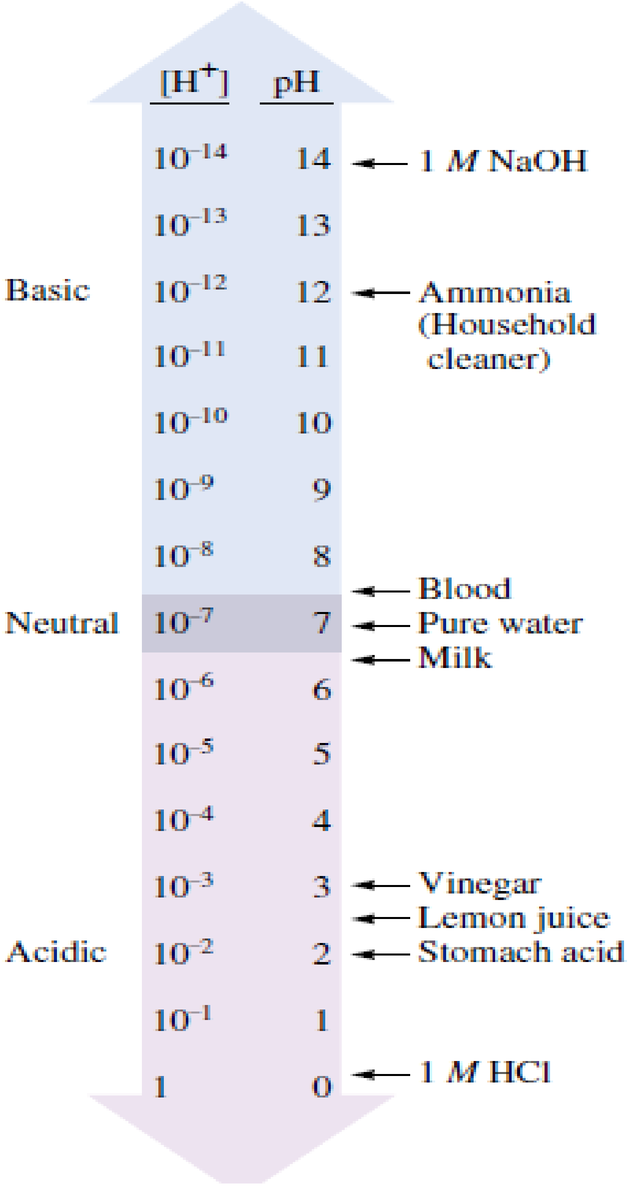
$$[H^+] = 1.0 \times 10^{-7}\ M$$
$$pH = -(-7.00) = 7.00$$

- Similar log scales are used for representing other quantities; for example,

$$pOH = -\log[OH^-]$$
$$pK = -\log K$$

- For *any* aqueous solution at 25^{0}C, pH and pOH add up to 14.00:

$$pH + pOH = 14.00$$



Sample Exercise 8.3

- Calculate pH and pOH for each of the following solutions at 25^0C .
  - a) 1.0×10^{-3} *M OH*⁻
  - b) 1.0 *M* H^+

- ***Solution***

a.

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\ M$$

$$pH = -\log[H^+] = -\log(1.0 \times 10^{-11}) = 11.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-3}) = 3.00$$

b.

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14}\ M$$

$$pH = -\log[H^+] = -\log(1.0) = 0.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-14}) = 14.00$$

Sample Exercise 8.4

- The pH of a sample of human blood was measured to be 7.41 at . Calculate pOH, $[H^+]$, and $[OH^-]$ for the sample.
- ***Solution***

Since pH + pOH = 14.00,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 7.41 = 6.59$$

To find $[H^+]$ we must go back to the definition of pH:

$$\text{pH} = -\log[H^+]$$

$$[H^+] = \text{antilog}(-\text{pH})$$

$$[H^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-7.41) = 10^{-7.41} = 3.9 \times 10^{-8}$$

Similarly, $[OH^-] = \text{antilog}(-\text{pOH})$, and

$$[OH^-] = \text{antilog}(-6.59) = 10^{-6.59} = 2.6 \times 10^{-7}\ M$$

Sample Exercise 8.5

a. Calculate the pH of 0.10 M HNO_3.
b. Calculate the pH of 1.0×10^{-10} M HCl.

- ***Solution***

a. Since HNO_3 is a strong acid, the major species in solution are

$$H^+, \quad NO_3^-, \quad \text{and} \quad H_2O$$

The sources of H^+ are

1. H^+ from HNO_3 (0.10 M)
2. H^+ from H_2O

- The number of H^+ ions contributed by the autoionization of water will be very small compared with the 0.10 M contributed by the HNO_3 and can be neglected.

$$[H^+] = 0.10\ M \quad \text{and} \quad pH = -\log(0.10) = 1.00$$

b. Normally, in an aqueous solution of HCl the major species are H^+, Cl^-, and H_2O. However, in this case the amount of HCl in solution is so small that it has no effect; the only major species is H_2O. Thus the pH will be that of pure water, or pH = 7.00.

- Bases
  - Arrhenius: bases produce OH^- ions.
  - Brønsted–Lowry: bases are proton acceptors.
  - In a basic solution at 25° C, pH > 7.
  - Ionic compounds containing OH^- are generally considered strong bases.
    - $LiOH$, $NaOH$, KOH, $Ca(OH)_2$
- Because of their complete dissociation, NaOH and KOH are called strong bases

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

Sample Exercise 8.6

Calculate the pH of a $5.0 \times 10^{-2}\,M$ NaOH solution.

Solution

The major species in this solution are

$$\underbrace{Na^+, \quad OH^-,}_{\text{From NaOH}} \quad \text{and} \quad H_2O$$

Although autoionization of water also produces OH^- ions, the pH will be dominated by the OH^- ions from the dissolved NaOH. Thus, in the solution,

$$[OH^-] = 5.0 \times 10^{-2}\,M$$

and the concentration of H^+ can be calculated from K_w:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 - 10^{-13}\,M$$

$$pH = 12.70$$

Note that this is a basic solution for which

$$[OH^-] > [H^+] \quad \text{and} \quad pH > 7$$

❖Polyprotic acids

- Acids that can furnish more than one proton.
- such as sulfuric acid (H_2SO_4- diprotic acid) and phosphoric acid (H_3PO_4-triprotic acid)
- Always dissociates in a stepwise manner, one proton at a time.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \quad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

- The conjugate base of the first dissociation equilibrium becomes the acid in the second step.
- For a typical weak polyprotic acid:

$$K_{a1} > K_{a2} > K_{a3}$$

- For a typical polyprotic acid in water, only the first dissociation step is important to pH.

- Salts
  - Ionic compounds.
  - When dissolved in water, break up into its ions (which can behave as acids or bases).
  - The salt of a strong acid and a strong base gives a neutral solution.
    - KCl, $NaNO_3$
  - A basic solution is formed if the anion of the salt is the conjugate base of a weak acid.
    - NaF, $KC_2H_3O_2$
  - An acidic solution is formed if the cation of the salt is the conjugate acid of a weak base.
    - NH_4Cl

Section 8.7

Acid-Base Properties of Salts

CATION	ANION	ACIDIC OR DASIC	EXAMPLES
neutral	neutral	neutral	NaCL
neutral	Conjugate base of weak acid	base	NaF
Conjugate acid of weak base	neutral	acidic	NH_4Cl

- **The Lewis Acid–Base Model**

Lewis acid is an electron-pair acceptor.

Lewis base is an electron-pair donor.

TABLE 14.10 Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor