

CHAPTER 5

EQUILIBRIUM PROBLEMS IN COMPLEX SYSTEMS:

APPLICATION OF EQUILIBRIUM CALCULATIONS TO COMPLEX SYSTEMS, SYSTEMATIC METHOD FOR SOLVING MULTIPLE EQUILIBRIUM PROBLEMS, SOLUBILITY EQUILIBRIUM CALCULATIONS

In this chapter,

- ❖ **chemical equilibrium** including calculations of **chemical composition** and of **equilibrium concentrations** for monoprotic acid/base systems will be considered.
- ❖ **buffer solutions**, which are extremely important in many areas of science, and describe the properties of these solutions will be discussed.

THE CHEMICAL COMPOSITION OF AQUEOUS SOLUTIONS

Electrolytes form **ions** when dissolved in water (or certain other solvents) and thus produce solutions that **conduct electricity**.

Strong electrolytes ionize essentially **completely** in a solvent,
Weak electrolytes ionize only **partially**.

**Conducting electricity by weak electrolytes <<< strong
electrolyte**

TABLE 9-1**Classification of Electrolytes****Strong**

1. Inorganic acids such as HNO_3 , HClO_4 , H_2SO_4^* , HCl , HI , HBr , HClO_3 , HBrO_3
2. Alkali and alkaline-earth hydroxides
3. Most salts

Weak

1. Many inorganic acids, including H_2CO_3 , H_3BO_3 , H_3PO_4 , H_2S , H_2SO_3
2. Most organic acids
3. Ammonia and most organic bases
4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

* H_2SO_4 is completely dissociated into HSO_4^{2-} and H_3O^+ ions and for this reason is classified as a **strong electrolyte**.

HSO_4^{2-} ion is a **weak electrolyte** and is only partially dissociated into SO_4^{2-} and H_3O^+ .

Brønsted-Lowry Theory

An **acid** donates protons.

only in the presence of a proton acceptor (**base**).

A **base** is a proton acceptor.

only in the presence of a proton donor (**acid**).

A **salt** is produced in the reaction of an acid with a base.

NaCl, Na₂SO₄, NaOOCCH₃

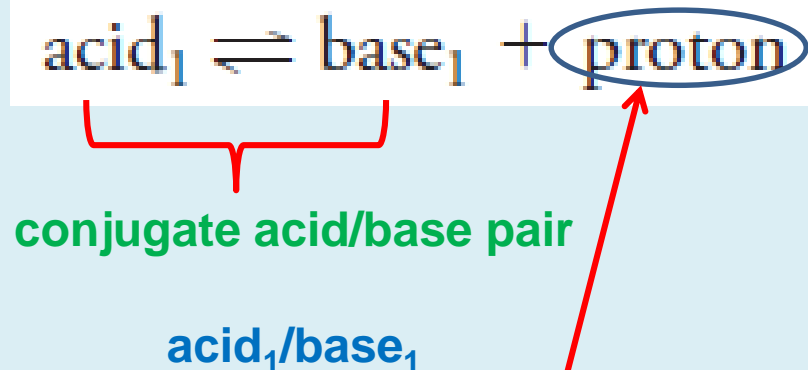
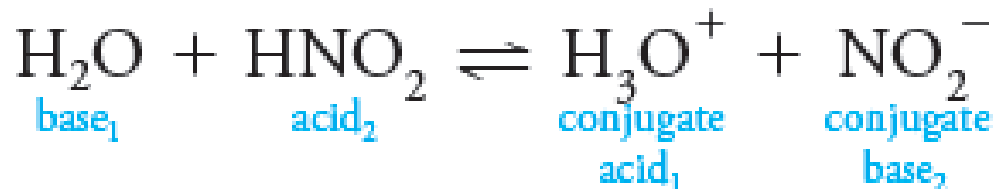
Arrhenius acid-base definition

(acid produces H₃O⁺ and base forms OH⁻ in water.)

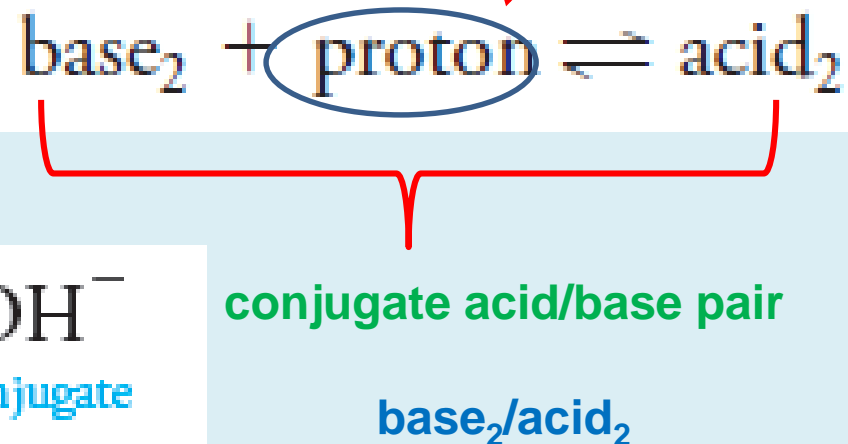
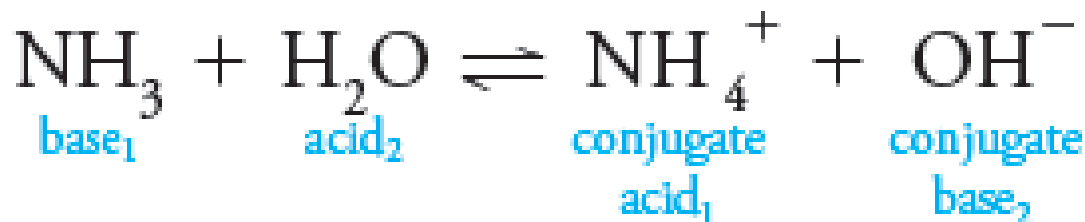
Lewis acid-base definition

(acid accepts and shares electron and bases share their electrons)

A **conjugate base** is formed when an **acid** loses a proton.

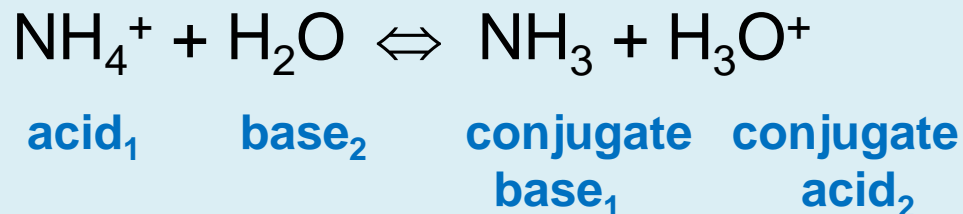
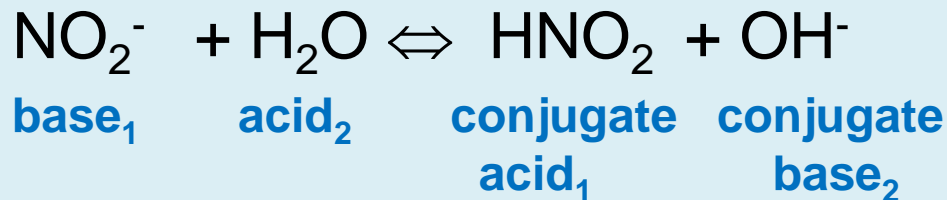
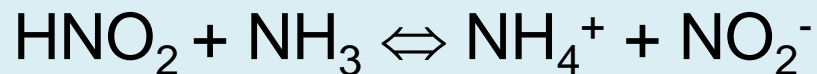


A **conjugate acid** is formed when an **base** gains a proton.



A substance acts as an acid only in the presence of a base and vice versa.

Neutralization:



Amphiprotic Species

Species that have both **acidic** and **basic** properties are **amphiprotic**.

- ❖ behaves as a **base** in the presence of a proton donor.



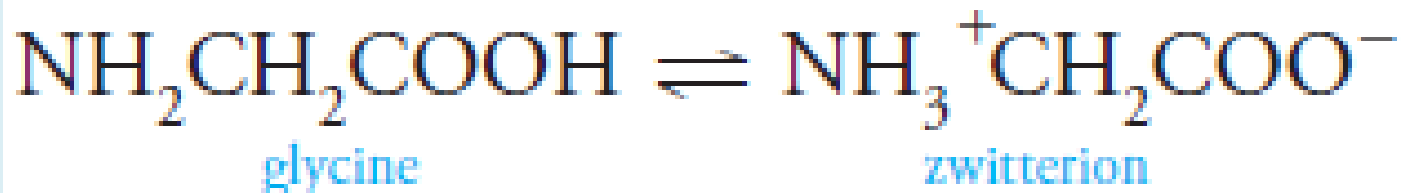
- ❖ behaves as an **acid** in the presence of a proton acceptor.



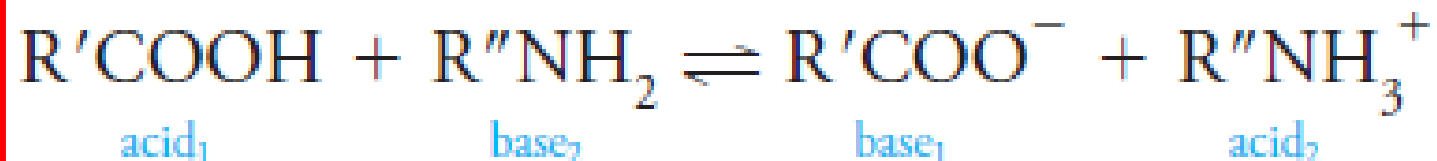
Water acts as a proton acceptor (base) and as a proton donor (acid):
Amphiprotic solvent

The simple **amino acids** are an important class of **amphiprotic compounds** that contain both a weak acid and a weak base functional group.

an amino acid, undergoes a kind of **internal acid/base reaction** to produce a **zwitterion**—a species that has both a **positive** and a **negative** charge.

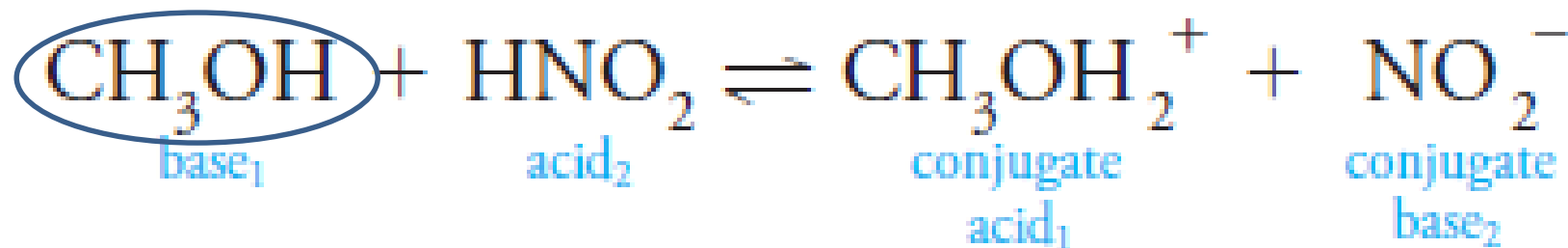
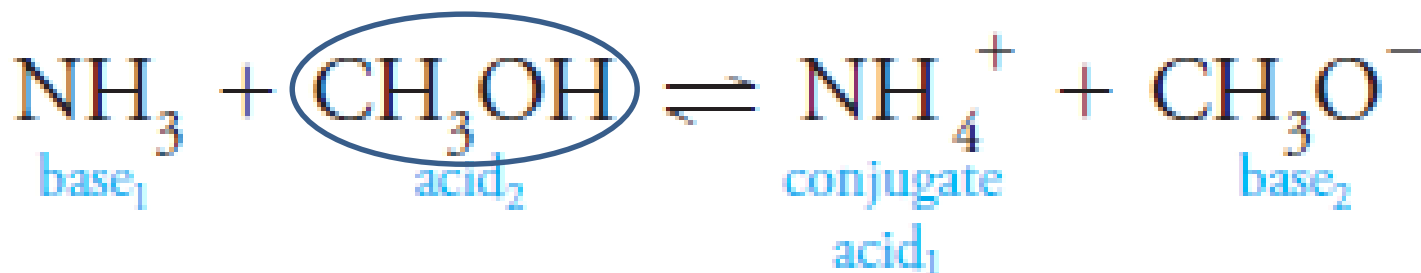


acid/base reaction between a carboxylic acid and an amine



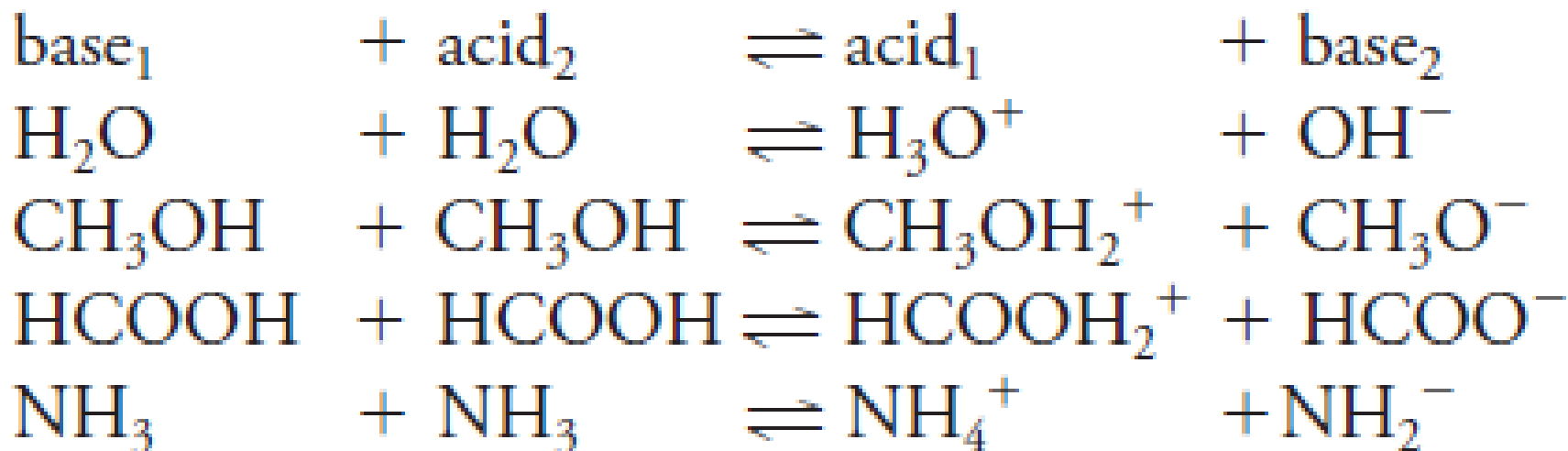
Water acts as a proton acceptor (base) and as a proton donor (acid):
Amphiprotic solvent

Other common amphiprotic solvents are **methanol**, **ethanol**, and **anhydrous acetic acid**.



Autoprotolysis (autoionization)

Amphiprotic solvents undergo **self-ionization**, or **autoprotolysis**, to form a pair of ionic species.



Water slightly undergoes autoprotolysis at room temperature. Thus, the hydronium (H_3O^+) and hydroxide ion (OH^-) concentrations in pure water are only about 10^{-7} M.

Strengths of Acids and Bases

strong acids: reaction with the solvent is sufficiently complete that **no undissociated solute molecules** are left in aqueous solution.

weak acids: react incompletely with water to give solutions containing significant quantities of both the parent acid and its conjugate base.

Note that acids can be **cationic, anionic, or electrically neutral**.
The same holds for bases.

The **common strong acids** include HCl, HBr, HI, HClO₄, HNO₃, the first proton in H₂SO₄, and the organic sulfonic acid RSO₃H.

The **common strong bases** include NaOH, KOH, Ba(OH)₂, and the quaternary ammonium hydroxide R₄NOH, where R is an alkyl group such as CH₃ or C₂H₅.

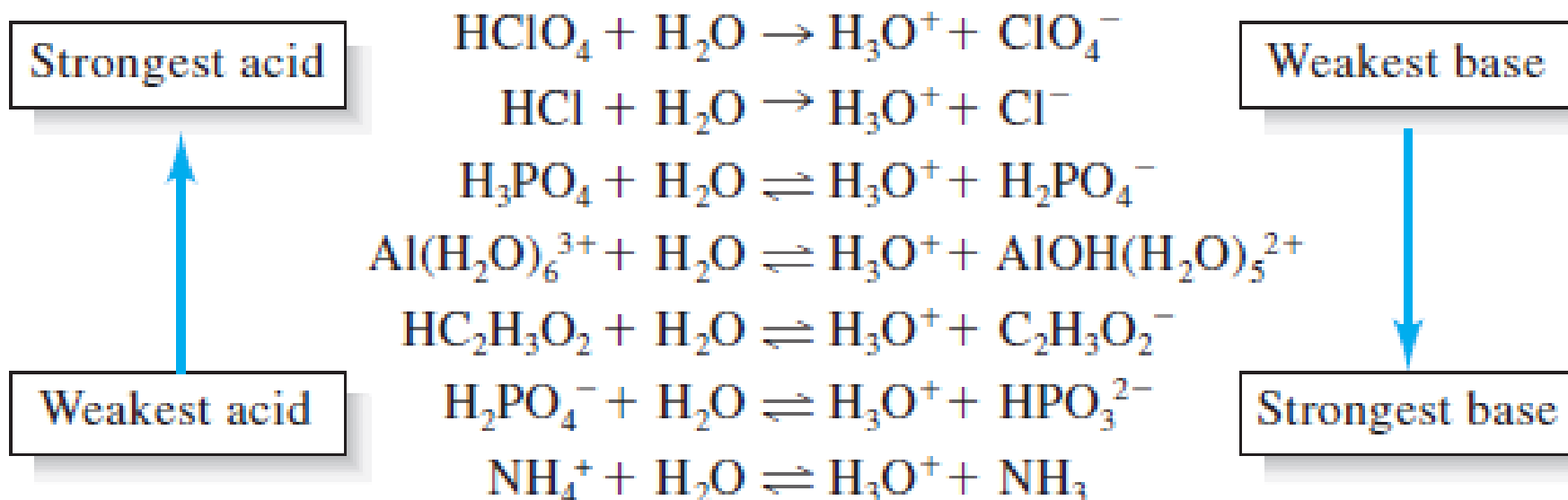
Conjugate acids/bases of **strong acids/bases** **do not undergo a hydrolysis reaction**. They are not strong enough to produce hydronium (H_3O^+) and hydroxide ion (OH^-).

Conjugate acids/bases of **weak acids** are strong enough to undergo a **hydrolysis reaction**. They produce hydronium (H_3O^+) or hydroxide ion (OH^-) and change the pH of the solution.

Note that acids can be **cationic, anionic, or electrically neutral**.
The same holds for bases.

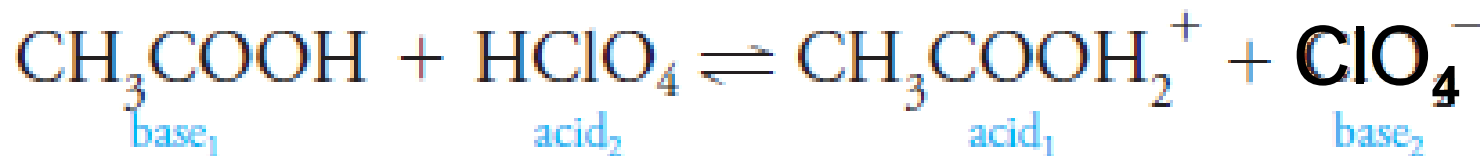
The tendency of a solvent to accept or donate protons determines the **strength of a solute acid or base** dissolved in it.

Water, is a **leveling solvent** for perchloric, hydrochloric, and nitric acids because all three are **completely ionized** in this solvent and show no differences in strength.



In a **leveling solvent**, several acids are **completely dissociated** and show the same strength.

Anhydrous acetic acid acts as a **differentiating solvent** toward the two acids by revealing the inherent differences in their acidities.



Perchloric acid is, however, about 5000 times **stronger than hydrochloric acid** in this solvent.

We conclude that :

- ❖ anhydrous acetic acid, is a weaker proton acceptor than water,
- ❖ neither of HCl and HClO₄ undergoes complete dissociation.
- ❖ Instead, equilibria such as the above mentioned are established.

In a **differentiating solvent**, various acids **dissociate to different degrees** and have different strengths.

“Only perchloric acid is a strong acid in **methanol and ethanol**. Therefore, these two alcohols are also **differentiating solvents**.”

CHEMICAL EQUILIBRIUM

Many reactions used in analytical chemistry never result in complete conversion of reactants to products.

They proceed to a state of **chemical equilibrium** in which the ratio of concentrations of reactants and products is **constant**.

Equilibrium- constant expressions:

- ❖ describe the concentration relationships among reactants and products at equilibrium.
- ❖ permit calculation of the error in an analysis resulting from the quantity of unreacted analyte that remains when equilibrium has been reached.

The Equilibrium State



We can follow the rate of this reaction and the extent to which it proceeds to the right by monitoring the appearance of the **orange-red color of the triiodide ion I_3^-** .

A solution of **identical color** intensity can be produced by using appropriate amount of reactants for both reactions.

The final position of a chemical equilibrium is **independent** of the route to the equilibrium state.

the **concentration relationship** at chemical equilibrium (that is, the *position of equilibrium*) is independent of the route to the equilibrium state.

This relationship is altered by **applying stress** to the system.

Such stresses include changes in **temperature**, in **pressure** (if one of the reactants or products is a gas), or in **total concentration** of a reactant or a product.

These effects can be predicted qualitatively from the **Le Châtelier's principle**.

The **mass-action effect** is a shift in the position of an equilibrium caused by adding one of the reactants or products to a system.

This principle states that **the position of chemical equilibrium always shifts in a direction that tends to relieve the effect of an applied stress**.

Equilibrium is a dynamic process.

Although chemical reactions appear to stop at equilibrium, in fact, the amounts of reactants and products are constant because the **rates of the forward and reverse processes are exactly the same.**

Chemical thermodynamics is a branch of chemistry that **concerns the flow of heat and energy** in chemical reactions. The position of a chemical equilibrium is related to these energy changes.

Equilibrium-Constant Expressions



$$K = \frac{[Y]^y [Z]^z}{[W]^w [X]^x}$$

where the square-bracketed terms are:

1. **molar concentrations** if they represent dissolved solutes.
2. **partial pressures in atmospheres** if they are gas-phase reactants or products.

In such an instance, we will often replace the square bracketed terms with the symbol ***p***, which stands for *the partial pressure* of the gases in atmospheres.

If a reactant or product is a **pure liquid**, a **pure solid**, or the **solvent** present in excess, **no term** for this species appears in the equilibrium-constant expression.

$$K = \frac{[Y]^y [Z]^z}{[W]^w [X]^x}$$

Approximate Equilibrium constants

$$K = \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

Exact Equilibrium constants
(thermodynamic)

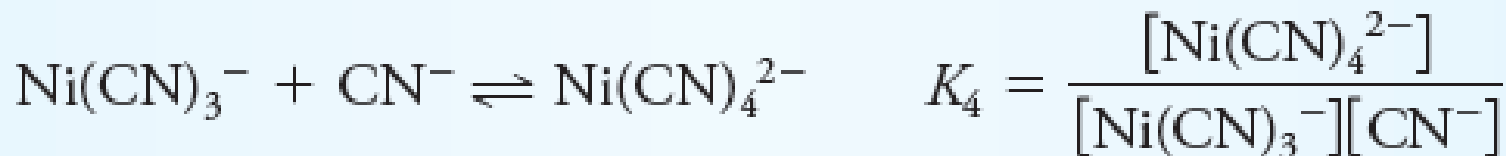
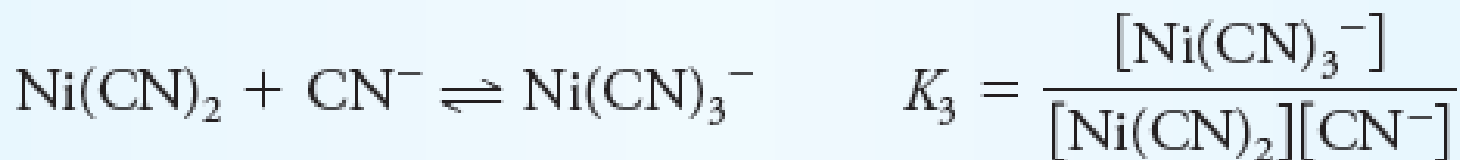
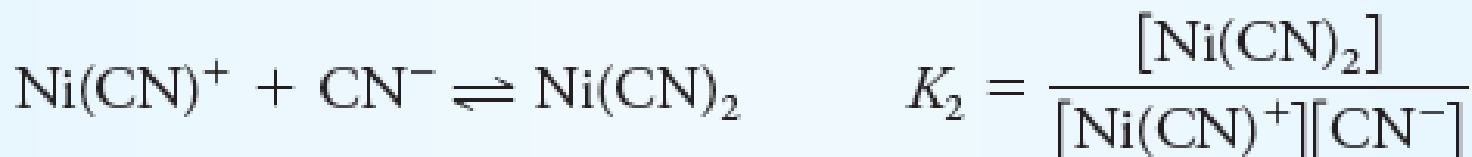
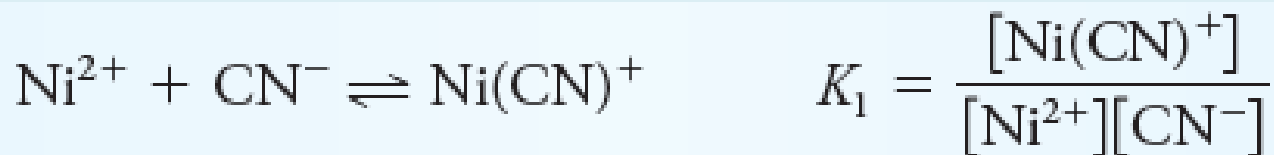
Types of Equilibrium Constants in Analytical Chemistry

TABLE 9-2

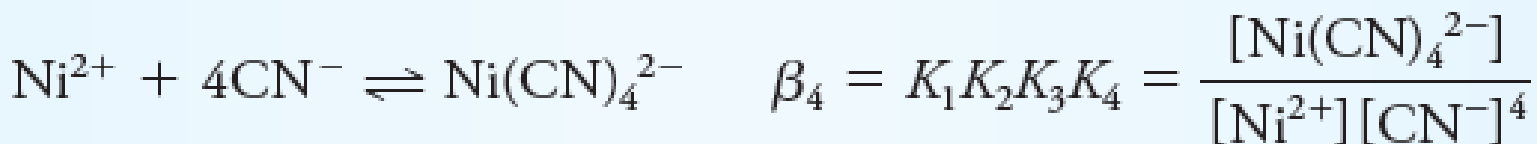
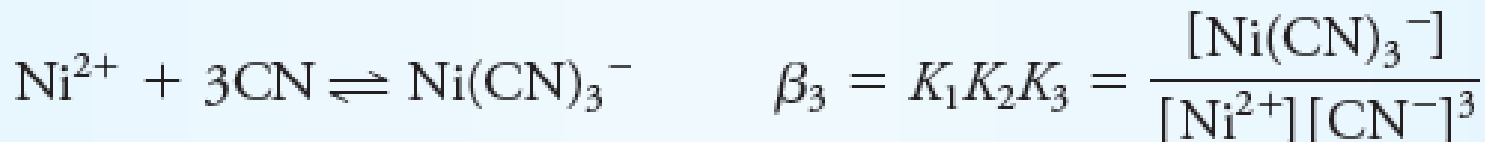
Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Ion-product constant, K_w Solubility product, K_{sp}	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$ $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH}$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ $K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$
Formation of a complex ion	Formation constant, β_n	$\text{Ni}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-}$	$\beta_4 = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$	$K_{\text{redox}} = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$\text{I}_2(aq) \rightleftharpoons \text{I}_2(org)$	$K_d = \frac{[\text{I}_2]_{org}}{[\text{I}_2]_{aq}}$

The formation of $\text{Ni}(\text{CN})_4^{2-}$ is typical in that it occurs in steps as shown. **stepwise formation constants are: K_1, K_2, \dots**



Overall constants are designated by the symbol β_n .



Applying the Ion-Product Constant for Water

Aqueous solutions contain small concentrations of **hydronium** and **hydroxide ions** as a result of the dissociation reaction.



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

$$K[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

ion-product constant for water

$$-\log K_w = -\log[\text{H}_3\text{O}^+] - \log [\text{OH}^-]$$

$$p K_w = pH + pOH \quad \text{At } 25^\circ\text{C}, pK_w = 14.00.$$

TABLE 9-3

Variation of K_w with Temperature

Temperature, °C	K_w
0	0.114×10^{-14}
25	1.01×10^{-14}
50	5.47×10^{-14}
75	19.9×10^{-14}
100	49×10^{-14}

Why [H₂O] Does Not Appear in Equilibrium-Constant Expressions for Aqueous Solutions

In a dilute aqueous solution, the molar concentration of water is

$$[\text{H}_2\text{O}] = \frac{1000 \text{ g H}_2\text{O}}{\text{L H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 55.6 \text{ M}$$

If we have 0.1 mol of HCl in 1 L of water. The presence of this acid will shift the equilibrium to the left.



Originally, however, there was only 10^{-7} mol/L OH⁻ to consume the added protons.

Therefore, even if all the OH⁻ ions are converted to H₂O, the water concentration will increase to only

$$[\text{H}_2\text{O}] = 55.6 \frac{\text{mol H}_2\text{O}}{\text{L H}_2\text{O}} + 1 \times 10^{-7} \frac{\text{mol OH}^-}{\text{L H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{\text{mol OH}^-} \approx 55.6 \text{ M}$$

$$\frac{10^{-7} \text{ M}}{55.6 \text{ M}} \times 100\% = 2 \times 10^{-7}\%$$

The percent change in water concentration is insignificant.

$$K(55.6)^2 = K_w = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

The ion-product constant for water permits us to **easily find the hydronium and hydroxide ion concentrations** of aqueous solutions.

Applying the ION-PRODUCT constant for water

Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C .

Answers:

$$\text{At } 25^\circ\text{C} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$$

$$\text{At } 100^\circ\text{C} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-] = 7.00 \times 10^{-7} \text{ M}$$

EXAMPLE : Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of **0.013 M** aqueous KOH at 25 °C.

EXAMPLE : Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of **1.30×10^{-7} M** aqueous KOH at 25 °C.

EXAMPLE : Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of **0.023 M** aqueous HNO_3 at $25\text{ }^\circ\text{C}$.

EXAMPLE : Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of **2.30×10^{-7} M** aqueous HNO_3 at $25\text{ }^\circ\text{C}$.

USING ACID/BASE DISSOCIATION CONSTANTS

- 1. Dissociation Constants for Conjugate Acid/Base Pairs**
- 2. Hydronium Ion Concentration of Solutions of Weak Acids**
- 3. Hydronium Ion Concentration of Solutions of Weak Bases**

Using Solubility-Product Constants

1. The Solubility of a Precipitate in Pure Water

2. The Effect of a Common Ion on the Solubility of a Precipitate