AL- MUSTAQBAL UNIVERSITY College Of Health And Medical Techniques Prosthetic Dental Techniques Department Second Grade Second Semester



Advanced chemistry

Lecture 6 (The theoretical part)

(Aqueous Solutions and Chemical Equilibrium)

By:

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4.Aqueous Solutions and Chemical Equilibrium

Water is the most plentiful solvent on Earth, is easily purified, and is not toxic. It is, therefore, widely used as a medium for chemical analyses.

4.1. Classifying Solutions of Electrolytes

Most of the solutes we will discuss are **electrolytes**, which 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, but **weakelectrolytes** ionize only partially. These characteristics mean that a solution of a weak electrolyte will not conduct electricity as well as a solution containing an equal.

Strong	Weak
 Inorganic acids such as HNO₃, HClO₄, H₂SO₄*, HCl, HI, HBr, HClO₃, HBrO₃ Alkali and alkaline-earth hydroxides Most salts 	 Many inorganic acids, including H₂CO₃, H₃BO₃, H₃PO₄, H₂S, H₂SO₃ Most organic acids Ammonia and most organic bases Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

 $^{*}H_{2}SO_{4}$ is completely dissociated into HSO_{4}^{-} and $H_{3}O^{+}$ ions and for this reason is classified as a strong electrolyte. Note, however, that the HSO_{4}^{-} ion is a weak electrolyte and is only partially dissociated into SO_{4}^{2-} and $H_{3}O^{+}$.

4.2. Chemical Equilibrium

Many reactions used in analytical chemistry never result in complete conversion of reactants to products. Instead, they proceed to a state of **chemical equilibrium** in which the ratio of concentrations of reactants and products is constant. **Equilibrium-constant expressions** are *algebraic* equations that describe the concentration relationships among reactants and products at equilibrium. Among other things, equilibrium-constant expressions permit calculation of the error in an analysis resulting from the quantity of unreacted analyte that remains when equilibrium has been reached. In the discussion that follows, we cover the use of equilibrium-constant expressions to gain information about analytical systems in which no more than one or two equilibria are present.

4.2.1. The Equilibrium State

Consider the chemical reaction

$$\begin{split} H_3AsO_4 + 3I^- + 2H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O \\ H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H^+ \end{split}$$

Le Châtelier's principle: states that the position of an equilibrium always shifts in such a direction as to relieve a stress that is applied to the system.

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.

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.

4.2.2. Equilibrium-Constant Expressions

Equilibrium-constant expressions provide *no* information about whether a chemical reaction is fast enough to be useful in an analytical procedure. Consider a generalized equation for a chemical equilibrium

$$wW + xX \rightleftharpoons yY + zZ$$

where the capital letters represent the formulas of participating chemical reactants and products, and the lowercase italic letters are the small whole numbers required to balance the equation. Thus, the equation says that w moles of W react with xmoles of X to form y moles of Y and z moles of Z. The equilibrium-constant expression for this reaction is

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

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 term with the symbol pz, which stands for the partial pressure of the gas Z in atmospheres.

4.2.3. Applying the Ion-Product Constant for Water

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

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

An equilibrium constant for this reaction can be written as shown in Equation

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The concentration of water in dilute aqueous solutions is enormous, however, when compared with the concentration of hydronium and hydroxide ions. As a result, $[H_2O]_2$ in Equation below can be taken as constant, and we write

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

where the new constant *K*w is given a special name, the **ion-product constant for water**.

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

Solution

Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

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

We substitute this equality into Equation 9-11 to give

$$[H_3O^+]^2 = [OH^-]^2 = K_w$$

 $[H_3O^+] = [OH^-] = \sqrt{K_w}$

At 25°C,

$$[H_3O^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} M$$

At 100°C, from Table 9-3,

$$[H_3O^+] = [OH^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7} M$$

Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of 0.200 M aqueous NaOH at 25°C.

Solution

Sodium hydroxide is a strong electrolyte, and its contribution to the hydroxide ion concentration in this solution is 0.200 mol/L. As in Example 9-1, hydroxide ions and hydronium ions are formed in equal amounts from the dissociation of water. Therefore, we write

$$[OH^{-}] = 0.200 + [H_3O^{+}]$$

where [H₃O⁺] is equal to the hydroxide ion concentration from the dissociation of water. The concentration of OH⁻ from the water is insignificant, however, compared with 0.200, so we can write

$$[OH^-] \approx 0.200$$

 $POH = -\log 0.200 = 0.699$

Equation 9-11 is then used to calculate the hydronium ion concentration:

$$[H_{3}O^{+}] = \frac{K_{w}}{[OH^{-}]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14} \text{ M}$$

pH = -log 0.500 × 10⁻¹⁴ = 13.301

Note that the approximation

$$[OH^{-}] = 0.200 + 5.00 \times 10^{-14} \approx 0.200 \text{ M}$$

causes no significant error in our answer.

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- Chemical Equilibrium
- The Equilibrium State
- Equilibrium-Constant Expressions
- Applying the Ion-Product Constant for Water

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