جامعة الانبار كلية : الصيدلة قسم : الكيمياء الصيدلانية اسم المادة باللغة العربية: الكيمياء التحليلية اسم المادة باللغة العربية: الكيمياء التحليلية مسم المادة باللغة الإنكليزية: الكولى المرحلة: الاولى عنوان المحاضرة باللغة العربية: التوازن الكيميائي عنوان المحاضرة باللغة الإنكليزية : Chemical Equilibrium

4.1 Introduction

The 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 existing 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.

4.2 Equilibrium Constant Expressions

The influence of concentration (or pressure if the species are gases) on the position of a chemical equilibrium is conveniently described in quantitative terms by means of an *equilibrium-constant expression*. Such expressions are derived from thermodynamics. They are important because they permit the chemist to predict the direction and completeness of a chemical reaction. An equilibrium-constant expression, however, yields no information concerning the rate at which equilibrium is approached. In fact, we sometimes encounter reactions that have highly favorable equilibrium constants but are of little analytical use because their rates are low. This limitation can often be overcome by the use of a catalyst, which speeds the attainment of equilibrium without changing its position.

For the reaction:

$$mA + nB = yC + zD$$

the equilibrium constant is:

$$K_{\mathbf{c}} = \frac{[\mathbf{C}]^{\mathbf{y}}[\mathbf{D}]^{\mathbf{z}}}{[\mathbf{A}]^{\mathbf{m}}[\mathbf{B}]^{\mathbf{n}}}$$

where K_c is the equilibrium constant, the letter c denote the concentrations in mole/liter. The square-bracketed terms mean the molar concentration if the species is a dissolved solute. And mean partial pressure in atmospheres if the species is a gas; in fact, we often replace K_c with K_p in this case. K_c is large if the products more than reactants, and small if the products less than reactants, and equal to 1 if the concentrations of the products and reactants are equal at the equilibrium state.

Example 1

Write the equilibrium constant for the following reactions:

1-
$$2NO_{(g)} + Cl_{2(g)} = 2NOCl_{(g)}$$

2- $Na_2CO_{3(s)} + BaSO_{4(s)} = Na_2SO_{4(s)} + BaCO_{3(s)}$
 $[NOCl_{(g)}]^2$

1-
$$K_{\rm p} = \frac{[{\rm NO}_{({\rm g})}]^2}{[{\rm NO}_{({\rm g})}]^2 [{\rm Cl}_{2({\rm g})}]}$$

2-
$$K_{c} = \frac{[Na_{2}SO_{4(s)}][BaCO_{3(s)}]}{[Na_{2}CO_{3(s)}][BaSO_{4(s)}]}$$

Example 2

In the thermal cracking of HI at 321.4° C, the premier concentration of the substance was 2.08 *M*, and in the equilibrium state the concentration was 1.68*M*. Calculate *K*_c.

$$2\mathrm{HI}_{(\mathrm{g})} = H_{2(\mathrm{g})} + \mathrm{I}_{2(\mathrm{g})}$$

at the beginning of the reaction the concentration of HI was 2.08 M, then become 1.68 M in the equilibrium state, so the disappeared quantity is:

$$2.08 - 1.68 = 0.40 M$$

If we go back to the balanced equation we find that the disappearance of 2 mole from HI gives 1 mole from H₂ and 1 mole from I₂, then the concentration of H₂ and I₂ at the equilibrium 0.40/2 = 0.2, so:

the concentration at the beginning2.0800the concentration at the equilibrium1.680.200.20

$$K_{\rm c} = \frac{(0.20)(0.20)}{(1.68)^2} = 0.014 = 1.4 \text{ x } 10^{-2}$$

4.3 Dissociation of Water

or

Water is weak electrolyte, and the aqueous solutions contain small concentrations of hydronium H_3O^+ , and hydroxide OH^- ions as a consequence of the dissociation reaction:

$$2H_2O_{(1)(aq)} + OH_{(aq)} + O_3H$$

The equilibrium constant of this reaction is:

$$K_{\rm eq} = \frac{[{\rm H}^+][{\rm OH}^-]}{[{\rm H}_2{\rm O}]}$$

The concentration of water in dilute aqueous solutions is enormous when compared with the concentration of hydrogen and hydroxide ions. As a consequence, $[H_2O]$ in the equation can be taken as constant:

$$K_{\rm eq} \, [{\rm H}_2{\rm O}] = K_{\rm w} = [{\rm H}^+][{\rm O}{\rm H}^-]$$

Where K_w is the *ion-product constant* for water.

At 25°C, the ion-product constant for water is 1.00×10^{-14} , so:

 $[H_3O^+] = 1.0 \times 10^{-7} M$ $[OH^-] = 1.0 \times 10^{-7} M$

Example 3

If the concentration of OH^- ion in an ammonia solution was 0.0025 *M*, calculate the concentration of H^+ ion.

$$K_{\rm w} = [{\rm H}^+][{\rm OH}^-]$$
$$[{\rm H}^+] = \frac{K_{\rm w}}{[{\rm OH}^-]}$$
$$[{\rm H}^+] = \frac{1.0 \times 10^{-14}}{0.0025} = 4.0 \text{ x } 10^{-12} M$$

Example 4

In a $1.0 \times 10^{-4} M$ HCl solution, the concentration of hydrogen ions [H⁺] was 1.0×10^{-4} , calculate the hydroxide ions concentration. The ionization constant of water at 25°C is 1.0×10^{-14} .

$$K_{\rm w} = [{\rm H}^+][{\rm OH}^-]$$

$$1.0 \ge 10^{-14} = (1.0 \ge 10^{-4}) \text{ [OH}^{-1}$$

$$[OH^{-}] = \frac{1.0 \times 10^{-10} M}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$

4.4 pH Concept

Because the concentrations of H^+ and OH^- ions in aqueous solutions are very small, scientists invented the pH concept, which is the negative logarithm of hydrogen ion concentration in mole/liter. The negative logarithm gives positive number for the pH.

$$\mathbf{pH} = \log\left[\frac{1}{H^+}\right]$$

$$pH = -\log [H^+]$$

The pH is a measure of hydrogen ion concentration, so we can identify the solutions of acids and bases at 25°C by knowing the pH:

acidic solutions:	$[H^+] > 1.0 \times 10^{-7} M, \text{ pH} < 7.00$
basic solutions:	$[H^+] < 1.0 \times 10^{-7} M, \text{ pH} > 7.00$
neutral solutions:	$[H^+] = 1.0 \times 10^{-7} M, pH = 7.00$

The pOH is the negative logarithm of hydroxide ion concentration in the solution:

 $pOH = -\log [OH^{-}]$

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

If we take the negative logarithm for both sides of the equation, we get:

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

$$-\log [H^+] - \log [OH^-] = 14.00$$

From the definition of pH and pOH we get:

$$pH + pOH = 14$$

In neutral solution pH + pOH = 7

Example 5

The concentration of the hydrogen ion H^+ in a solution was 3.2×10^{-4} , calculate the pH of the solution.

$$pH = -\log [H^+]$$
$$= -\log (3.2 \times 10^{-4}) = 3.49$$

Example 6

The pH of a solution of acidic rain was 4.82. Calculate the concentration of H^+ ion for this solution.

pH =
$$-\log [H^+]$$

4.82 = $-\log [H^+]$
[H⁺] = 1.5 x 10⁻⁵ M

Example 7

Calculate the pH of a 0.10 M NaOH solution.

NaOH is a strong electrolyte, so the value of OH⁻ comes from the strong electrolyte.

$$[OH^{-}] = 0.10 M$$

$$K_{w} = [H^{+}][OH^{-}]$$

$$[H^{+}] = \frac{K_{w}}{[OH^{-}]}$$

$$[H^{+}] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} M$$

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

$$= -\log (1.0 \times 10^{-13}) = 13$$

Example 8

In a solution of NaOH, the concentration of OH⁻ ion was $2.9 \times 10^{-4} M$. Calculate the pH of the solution.

$$pOH = -\log [OH^{-}]$$

= - log (2.9 x 10⁻⁴)
= 3.54
$$pH + pOH = 14.00$$

$$pH = 14 - pOH$$

= 14 - 3.54 = 10.46

4.5 Dissociation of Weak Acids and Bases

When a weak acid or a weak base is dissolved in water, partial dissociation occurs. Thus if we assume that a weak acid HA dissociates according to the equation:

$$HA_{(aq)} + H_2O_{(aq)} = H_3O^+_{(aq)} + A^-_{(aq)}$$

or in a simpler way:

$$HA_{(aq)} = H^+_{(aq)} + A^-_{(aq)}$$

the equilibrium constant is:

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}$$

where K_a is the *acid-dissociation constant*. The stronger the acid the higher the value of K_a . Only weak acids have dissociation constant. Because the values of dissociation constants are very small, we use its logarithm, we call it mathematically pK_a .

$$pK_{\rm a} = -\log K_{\rm a}$$

Table 4-1 contains values of K_a for some weak acids.

Table 4-1 Values of K_a for some Weak Acids

<i>K</i> _a Value	Acid
4.5 x 10 ⁻⁴	$HNO_2 \longrightarrow H^+ + NO_2^-$ Nitrous acid
1.7 x 10 ⁻⁴	HCOOH \implies H ⁺ + HCOO ⁻ Formic acid
6.5 x 10 ⁻⁵	$C_6H_5COOH = H^+ + C_6H_5COO^-$ Benzoic acid
1.8 x 10 ⁻⁵	$CH_3COOH \longrightarrow H^+ + CH_3COO^-$ Acetic acid
6.2 x 10 ⁻¹⁰	HCN \longrightarrow H ⁺ + CN ⁻ Hydrocyanic acid

Weak polyprotic acids dissociate on steps, and each step has its own dissociation constant. Carbonic acid H_2CO_3 for example dissociates on two steps:

$$H_{2}CO_{3} = H^{+} + HCO_{3}^{-} \qquad K_{a1} = \frac{[H^{+}][HCO_{3}^{-}]}{[H_{2}CO_{3}]}$$
$$HCO_{3}^{-} = H^{+} + CO_{3}^{2-} \qquad K_{a2} = \frac{[H^{+}][CO_{3}^{2-}]}{[HCO_{3}^{-}]}$$

In an analogous way bases dissociate, and if a weak base dissolved in aqueous solution, it dissociates for small degree then reaches equilibrium:

 $B + H_2O \implies BH^+ + OH^-$

The dissociation constant is:

Note that a concentration term for water $([H_2O])$ does not appear in the denominator of either equation because it small and can be considered constant.

Example 9

Calculate K_a for acetic acid if premier concentration was 0.1 mol/L and the percentage of dissociation is 1.34%.

percentage of dissociation is 1.34, this means: in every 100 mole, 1.34 mole dissociate in every 0.1 mole X mole dissociate

$$X = \frac{1.34 \times 0.1}{00} = 0.00134$$

 $CH_3COOH \longrightarrow CH_3COO^- + H^+$

concentration at the beginning0.1000concentration at the equilibrium0.1-0.001340.001340.00134

$$K_{a} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$$
$$= \frac{(0.00134)(0.00134)}{0.10 - 0.00134}$$
$$= 1.82 \times 10^{-5}$$

Example 10

If the K_a for acetic acid is 1.8×10^{-5} , calculate the molar concentration for hydrogen ions [H⁺], and the dissociation percentage for 0.50 *M* acetic acid.

suppose *x* is the number of dissociated moles of acid per liter, so: x = number of H⁺ and CH₃COO⁻ moles produced per each liter, and (0.50 - x) = number of undissociated CH₃COOH moles per liter.

$$CH_3COOH \longrightarrow CH_3COO^- + H^+$$

concentration at the beginning0.5000concentration at the equilibrium0.50 - xxx

$$K_{a} = 1.8 \times 10^{-5} = \frac{[CH_{3}COO^{-}][H^{+}]}{[CH_{3}COOH]}$$
$$= \frac{(x)(x)}{0.50 - x}$$

The dissociation of weak acetic acid is very small, so the concentration of x is very small in contrast with the concentration of undissociated acid. In this example the value (0.50 - x) probably is very near to 0.50, so we can use a simple way and avoid using the quadratic equation:

$$1.8 \times 10^{-5} \approx \frac{(x)(x)}{0.50}$$
$$x^{2} \approx 0.90 \times 10^{-5} = 9.0 \times 10^{-6}$$
$$x \approx \sqrt{9.0} \times \sqrt{10^{-6}}$$
$$x \approx 3.0 \times 10^{-3} M = [\mathrm{H^{+}}]$$

it is also equal to the number of dissociated moles of acetic acid per liter.

number of moles at the start

$$=\frac{3.0\times10^{-3}}{0.50}=0.60\%$$

4.6 Complex Formation Constant

An analytically important class of reactions involves the formation of soluble complex ion. Example is:

where K_f is called the formation constant for the complex.

4.7 Oxidation-Reduction Equilibrium Constant

Equilibrium constant for oxidation-reduction reactions can be formulated in the usual way. For example:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H_3O^+ \implies 6Fe^{3+} + 2Cr^{3+} + 21H_2O$$

$$K = \frac{[\mathrm{Fe}^{3+}]^6 [\mathrm{Cr}^{3+}]^2}{[\mathrm{Fe}^{2+}]^6 [\mathrm{Cr}_2 \mathrm{O}_7^{2-}] [\mathrm{H}_3 \mathrm{O}^+]^{14}}$$

The concentration of water does not appear in the equilibrium since it is constant.

4.8 Le Chatelier's Principle

There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs. The rule, known as *Le Chatelier's principle*, state that *if an external stress is applied to a system at equilibrium, the system adjusts in such a way that* the stress is partially offset as the system reaches a new equilibrium position. The word stress here means a change in concentration, pressure, volume, or temperature that removes a system from the equilibrium state.

4.9 Factors Affect Chemical Equilibrium 1- Effect of pressure

Changes in pressure ordinary do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible. On the other hand, concentrations of gases are greatly affected by changes in pressure.

Suppose that the equilibrium system,

$$N_2O_4_{(g)} = 2NO_{2(g)}$$

is in a cylinder fitted with a movable piston. What happens if we increase the pressure on the gases by pushing down on the piston at constant temperature? Since the volume decreases, the concentration of both NO_2 and N_2O_4 increase. Because the concentration of NO_2 is squared in the equilibrium constant expression, the increase in pressure increases the numerator more than the denominator. The system is no longer at equilibrium.

2- Effect of temperature

The values of equilibrium are measured at certain temperature. Any change in temperature will change the equilibrium constant. For example, the formation of NO_2 from N_2O_4 is an endothermic process, and the reverse reaction is exothermic:

$$N_2O_4_{(g)} \rightarrow 2NO_{2(g)}$$

At equilibrium the net heat effect is zero because there is no net reaction. If the system is heated at constant volume more N_2O_4 will dissociate to NO_2 , and that shift the reaction to the right. In opposite, if the temperature is decreased, the reaction will shift to the left.

3- Effect of concentration

If we consider the equilibrium:

$CH_3COOH + H_2O = H_3O^+ + CH_3COO^-$

Any increase in H_3O^+ or CH_3COO^- concentration shifts the equilibrium to the left, and any increase in CH_3COOH concentration shifts the equilibrium to the right, but *K* remains constant.

4- Effect of catalyst

In an equilibrium system, a catalyst increases the speed of both forward and reverse reactions to the same extent. A catalyst does not change the relative amounts present at equilibrium; the value of the equilibrium constant is not changed. The catalyst dose change the time required for reaching the equilibrium. Reactions that require days or weeks to come to equilibrium may reach it in a matter of minutes in the presence of a catalyst.

4.10 Buffer Solutions

A solution that contains a weak acid plus a salt of that acid, or a weak base plus a salt of that base, has the ability to react with both strong acids and strong bases. Such a system is referred to as a buffer solution, because small additions of either strong acids or strong bases produce little change in the pH.

A simple buffer solution can be prepared by adding comparable molar amounts of acetic acid (CH₃COOH) and its salt sodium acetate (CH₃COONa) to water. This has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociate completely in water:

$$CH_3COONa_{(s)} \rightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

If an acid is added, the H⁺ ions will be consumed by the conjugate base in the buffer, CH₃COO⁻, according to the equation:

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightarrow CH_3COOH_{(aq)}$$

If a base is added to the buffer system, the OH⁻ ions will be neutralized by the acid in the buffer:

$$CH_3COOH_{(aq)} + OH_{(aq)} \rightarrow CH_3COO_{(aq)} + H_2O_{(l)}$$

In general, a buffer system can be represented as salt-acid or conjugate base-acid. Thus the sodium acetate-acetic acid buffer system can be written as CH₃COONa/CH₃COOH or simply CH₃COO⁻/CH₃COOH.

Thus:

(HCl + KCl) is not a buffer solution because HCl is a strong acid.

(H₃PO₄ + NaCl) is not a buffer solution because NaCl does not contain a conjugate base of H₃PO₄.

(H₂CO₃ + NaHCO₃) is a buffer solution because it contains a weak acid and its salt.

(CH₃COOH + CH₃COOK) is a buffer solution because it contains a weak acid and its salt.

4.11 Calculation of the pH of Buffer Solutions

The $[H_3O^+]$ in the *Ka* expression is used to determine the pH of a buffer.

Weak acid + H_2O \longrightarrow H_3O^+ + conjugate base

 $[H_{3}O^{+}][\text{conjugate base}]$ $K_{a} = \frac{[\text{weak acid}]}{[\text{weak acid}]}$ $[H_{3}O^{+}] = \frac{K_{a}[\text{weak acid}]}{[\text{conjugate base}]}$

$$pH = -\log [H_3O^+]$$

Example 11

What is the pH of a solution that is 0.400 M in formic acid and 1.00 M in sodium formate? HCOOH/HCOONa has a $K_a = 1.80 \times 10^{-4}$.

 $HCOOH_{(aq)} + H_2O_{(l)} = H_3O^+_{(aq)} + HCOO^-_{(aq)}$



 $pH = -\log(7.20 \times 10^{-5}) = 4.14$

4.12 Buffer Capacity

The buffer capacity of a solution is defined as the number of equivalents of strong acid or strong base needed to cause 1.00 liter of the buffer to undergo a 1.00-unit change in pH. The buffer capacity is dependent upon the concentration of the conjugated acid-base pair. It is also dependent upon their concentration ratio, and reaches maximum when this ratio is unity.