Al-Mustaqbal-College University

Chemical Engineering and Petroleum Industry Department

Analytical chemistry

First class / first term

Lecture Seven

By

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Lecture seven

- General Concepts Of Chemical Equilibrium

Even though in a chemical reaction the reactants may almost quantitatively react to form the products, reactions *never* go in only one direction. In fact, reactions reach an equilibrium in which the rates of reactions in both directions are equal. In this lecture we review the equilibrium concept and the equilibrium constant and describe general approaches for calculations using equilibrium constants. We discuss the activity of ionic species along with the calculation of activity coefficients.

3.1Chemical Reactions: The Rate Concept

In 1863 Guldberg and Waage described what we now call the law of mass action, which states that the rate of a chemical reaction is proportional to the "active masses" of the reacting substances present at any time. The active masses may be concentrations or pressures. Guldberg and Waage derived an equilibrium constant by defining equilibrium as the condition when the rates of the forward and reverse reactions are equal. Consider the chemical reaction

$$\mathbf{aA + bB \leftrightarrow cC + dD} \qquad \mathbf{(1)}$$

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According to Guldberg and Waage, the rate of the forward reaction is equal to a constant times the concentration of each species raised to the power of the number of molecules participating in the reaction that is:

$$\textbf{Rate}_{fwd} = k_{fwd}[A]a[B]b \qquad (2)$$

where rate fwd is the rate of the forward reaction and k_{fwd} is the rate constant, which is dependent on such factors as the temperature and the presence of catalysts. [A] and [B] represent the molar concentrations of A and B. Similarly, for the reverse reaction, Guldberg and Waage wrote

$$\textbf{Rate}_{rev} = k_{rev}[C]^c[D]^d \qquad (3)$$

and for a system at equilibrium, the forward and reverse rates are equal:

$$k_{fwd}[A]^a[B]^b = k_{rev}[C]^c[D]^d \qquad (4)$$

Rearranging these equations gives the molar equilibrium constant (which holds for dilute solutions) for the reaction, *K*:

$$\frac{k_{fwd}}{k_{rev}} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (5)$$

$$K = \frac{k_{fwd}}{k_{rev}} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (6)$$

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Chemical Equilibrium : State of a reaction mixture at which the forward reaction rate is equal to the reverse reaction rate.

There are two kinds of reactions:

1) Reversible reaction, $A + B \rightleftharpoons C + D$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

2) Irreversible reaction , $A + B \longrightarrow C + D$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Note : In generally, most of chemical reactions are consider as reversible reactions.

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There are two kinds of system :

a) Homogenous reactions : chemical reactions in which the reactants and products have the same phase (solid , liquid , gas)

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

$$2KOH_{(l)} + H_2C_2O_{4(l)} \longrightarrow K_2C_2O_{4(l)} + H_2O_{(l)}$$

b) Heterogeneous reactions : chemical reactions in which the reactants and products have more than phase .

$$FeS_{(s)} + HCl_{(l)} \longrightarrow FeCl_{2(l)} + H_2S_{(g)}$$

3.2 Types of Equilibria

We can write equilibrium constants for virtually any type of chemical process. Some common equilibria are listed in Table:1. The equilibria may represent dissociation (acid/base, solubility), formation of products (complexes), reactions (redox), a distribution between two phases (water and nonaqueous solvent—solvent extraction; adsorption from water onto a surface , etc.).

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Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acid dissociation constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

3.3 factors effecting the reaction at equilibrium

1) nature of reactant substances: depends upon crystal and molecular structure.

   Na is react much faster than Mg with water.

   Red phosphorus is react much faster than carbon.

2) Temperature: the speed of chemical reactions will increase with the increasing of temperature .

   There are two kinds of thermal reactions:

   a) Exothermic reaction, ΔH(-)

   b) Endothermic reaction, ΔH(+)

Increasing of temperature favour forward reaction.

Decreasing of temperature favour backward (reverse) reaction.

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3) Concentration: The rate of chemical reaction will increase with the increasing of concentration.

4) Solution and surface: Increasing the surface of the solution due to an increasing in rate of reaction.

5) Catalyst: There are two kinds of catalysts:

a) Positive catalyst: increase the rate of reaction.

b) Negative catalyst; decrease the rate of reaction.

6) Pressure: it use when we deals with gas: $CO+2H_2 \leftrightarrow 2CH_3OH$

Increasing of pressure will shift the reaction direction of less or lower volume this means, to forward direction. While; $H_2(g) + I_2(g) \leftrightarrow 2HI$

Increasing in pressure will not effect on this reaction because the volume of product equal to volume of reactant.

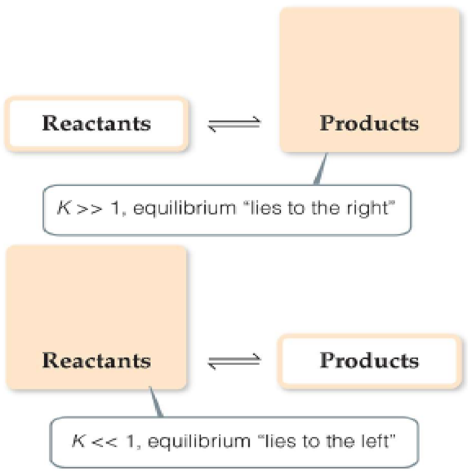
3.4 The Equilibrium Constant

For a reaction: $aA + bB \leftrightarrow cC + d$

equilibrium constant: $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

The **equilibrium constant, Kc,** is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

What Does the Value of K Mean?



- If $K>>1$, the reaction is *product-favored*; product predominates at equilibrium.
- If $K<<1$, the reaction is *reactant-favored*; reactant predominates at equilibrium.

*When $10^{-3} < K < 10^{3}$, the reaction is considered to contain a significant amount of both reactants and products at equilibrium.

Note : if K > 1 the reaction is forward (product to right)
If K < 1 the reaction is reverse (reactant to left)

<u>3.4.1Calculating Equilibrium Concentrations</u>

Use ICE Tables To Solve Equilibrium Problems For Kc Or Equilibrium Amounts:
1. I = initial concentration: Initial concentration of reactants are usually given; initial [Product]'s are assumed to be 0 unless otherwise specified.
2. C = change in concentration: Assign change as the variable x; use the stoichiometry of the reaction to assign changes for all species.
3. E = equilibrium concentration: E = I + C

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Example 1\\ In an analysis of the following reaction at 100°C

$$Br_{2(g)} + Cl_{2(g)} \leftrightarrow 2BrCl_{(g)}$$

the equilibrium concentrations are $[Br_2]= 2.3\text{x}10^{-3}$M,$[Cl_2] = 1.2 \text{ x } 10^{-2}$M, $[BrCl] = 1.4 \text{ x } 10^{-2}$ M. Write the equilibrium expression and calculate Kc for this reaction.

Solution:

$$K_c = \frac{[BrCL]^2}{[Br]_2[Cl]_2}$$

$$K_c = \frac{[1.4\times10^{-2}]^2}{[2.3\times10^{-3}][1.2\times10^{-2}]} = 7.1$$

Example 2\\ **The chemicals A and B react as follows to produce C and D:**

$A + B \leftrightarrow C + d$, $K = \frac{[D][C]}{[A][B]}$, The equilibrium constant K has a value of 0.30. Assume 0.20 mol of A and 0.50 mol of B are dissolved in 1.00 L, and the reaction proceeds. Calculate the concentrations of reactants and products at equilibrium.

Solve :

	[A]	[B]	[C]	[D]
Initial	0.20	0.50	0	0
Change (x = mmol/mL reacting)	$-x$	$-x$	$+x$	$+x$
Equilibrium	$0.20 - x$	$0.50 - x$	x	x

We can substitute these values in the equilibrium constant expression and solve for x:

$$K = \frac{[D][C]}{[A][B]}$$

$$0.3 = \frac{(x)(x)}{(0.2-x)(0.5-x)}$$

$$x^2 = (0.10 - 0.70x + x^2)0.30$$

$$0.70x^2 + 0.21x - 0.030 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-0.21 \pm \sqrt{(0.21)^2 - 4(0.70)(-0.030)}}{2(0.70)}$$

$$= \frac{-0.21 \pm \sqrt{0.044 + 0.084}}{1.40} = 0.11\ M$$

$[A] = 0.20 - x = 0.09M$

$[B] = 0.50 - x = 0.39M$

$[C] = [D] = x = 0.11M$

Example 3 Determine the initial concentration of HI if the initial concentrations of H_2 and I_2 are both 0.10 *M* and their equilibrium concentrations are both 0.043 *M* at 430°C. The value of Kc = 54.3

$$\mathbf{H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}}$$

Solution:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial	0.10	0.10	y
Change	-x	-x	+2x
Equilibrium	0.043	0.043	y + 2x

First solve for x: $0.10 - x = 0.043$; $x = 0.057$

Then solve for y: at equilibrium we have

$$K_c = 54.3 = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(y + 0.114)^2}{(0.043)(0.043)}$$

$$(y + 0.114)^2 = (54.3)(0.043)^2 \Rightarrow y = \sqrt{(54.3)(0.043)^2} - 0.114 = 0.203$$

Example 4 A closed system initially containing 1×10^{-3} M H_2 and 2×10^{-3} M I_2 at 448°C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate Kc at 448°C for the reaction taking place, which is : $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

solve :

1)	**H_2**	**I_2**	**2HI**
initial	**$1 * 10^{-3}$**	**$2 * 10^{-3}$**	**0**
change			
equilibrium			**$1.87 * 10^{-3}$**

2)

	H_2	I_2	$2HI$
initial	$1*10^{-3}$	$2*10^{-3}$	0
change	$-X$	$-X$	$+2X$
equilibrium	$1*10^{-3} - X$	$2*10^{-3} - X$	$1.87*10^{-3}$

$0+2X = 1.87 \times 10^{-3} \rightarrow X = 9.35 *10^{-4}$ M = [HI]

3)

	H_2	I_2	$2HI$
initial	$1 * 10^{-3}$	$2 * 10^{-3}$	0
change	$-9.35 *10^{-4}$	$-9.35 *10^{-4}$	$1.87 * 10^{-3}$
equilibrium	$1*10^{-3} - 9.35 *10^{-4}$	$2 * 10^{-3}-9.35 *10^{-4}$	$1.87 * 10^{-3}$

$[H_2] = 1*10^{-3} - 9.35 *10^{-4} = 6.5 * 10^{-5}$ M

$[I_2] = 2 * 10^{-3}-9.35 *10^{-4} = 1.065 * 10^{-3}$ M

$$K = \frac{[HI]^2}{[H_2]\,[I_2]} \rightarrow \frac{[1.87 * 10^{-3}]^2}{[6.5 * 10^{-5}]\,[1.065 * 10^{-3}]} = 51$$