



**Al-Mustaqbal-College University**  
**Chemical Engineering and Petroleum**  
**Industry Department**  
**Analytical chemistry**  
**First class / first term**  
**Lecture Three part 1**

**By**

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## Lecture three

### - 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.

### 3.1 Chemical 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



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:

$$\text{Rate}_{\text{fwd}} = k_{\text{fwd}}[A]^a[B]^b \quad (2)$$

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where rate fwd is the rate of the forward reaction and  $k_{\text{fwd}}$  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

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

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

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

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

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

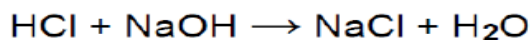
**Chemical Equilibrium :** State of a reaction mixture at which the forward reaction rate is equal to the reverse reaction rate.

There are two kinds of reactions:

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



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

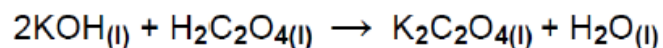
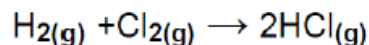


**Note : In generally, most of chemical reactions are consider as reversible reactions.**

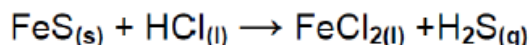
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There are two kinds of system :

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



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



### 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.).

#### Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$	$K_a$ , acid dissociation constant
Solubility	$\text{MA} \rightleftharpoons \text{M}^{n+} + \text{A}^{n-}$	$K_{\text{sp}}$ , solubility product
Complex formation	$\text{M}^{n+} + a\text{L}^{b-} \rightleftharpoons \text{ML}_a^{(n-ab)+}$	$K_f$ , formation constant
Reduction–oxidation	$\text{A}_{\text{red}} + \text{B}_{\text{ox}} \rightleftharpoons \text{A}_{\text{ox}} + \text{B}_{\text{red}}$	$K_{\text{eq}}$ , reaction equilibrium constant
Phase distribution	$\text{A}_{\text{H}_2\text{O}} \rightleftharpoons \text{A}_{\text{organic}}$	$K_D$ , distribution coefficient

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### 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,  $\Delta H(-)$

b) Endothermic reaction,  $\Delta H(+)$

# Increasing of temperature favour forward reaction.

# Decreasing of temperature favour backward (reverse) reaction.

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:  $\text{CO} + 2\text{H}_2 \leftrightarrow 2\text{CH}_3\text{OH}$

Increasing of pressure will shift the reaction direction of less or lower volume this means, to forward direction. While;  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}$

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