Analytical chemistry

Chemical engineering department

First class / first term

Al-Mustaqbal-college

Lecture Two

By

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Lecture Two

⇒ 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 , $A + B \longrightarrow C + D$

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

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

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 .

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

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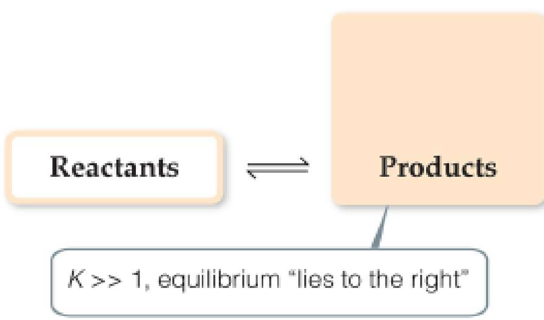
⇒ The Equilibrium Constant

For a reaction: aA + bB ↔ cC + d

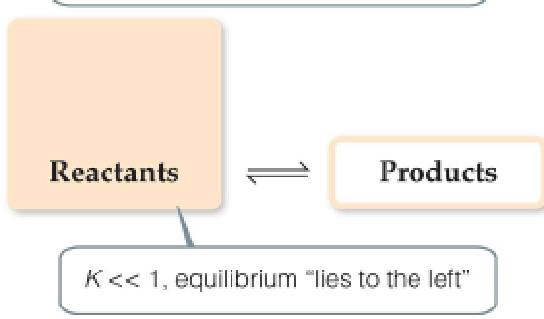
equilibrium constant: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

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.

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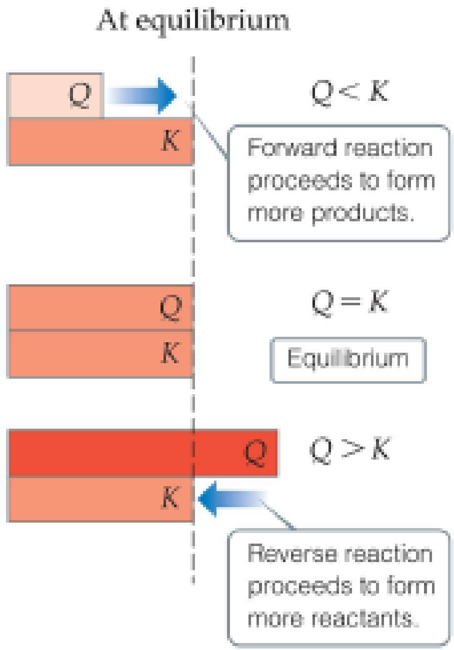
⇒Magnitude of Kc

The Reaction Quotient (Q)

- Q gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- To calculate Q, substitute the (*initial*) concentrations of reactants and products into the equilibrium expression.

$$aA + bB \rightleftharpoons cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$



Using Q and K to Predict the Direction of a Reaction

We can predict the direction of a reaction by comparing the values of Q and K.

$Q > K \Rightarrow$	**reverse reaction favored**
$Q = K \Rightarrow$	**equilibrium present**
$Q < K \Rightarrow$	**forward reaction favored**

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Factors effecting the reactions at equilibrium :

1) *nature of reactant substances* : depends upon the difference in 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 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) *Catalyste* : 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 :

$$CO + 2H_2 \rightleftharpoons 2CH_3OH$$

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Increasing of pressure will shift the reaction direction of less or lower volume this means, to forward direction.

While; $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI$

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

Equilibrium constant expressions :

Kw = ion product (or ionization) constant for water .

K.S.P = solubility product constant.

Ka = ionization (or dissociation) constant of a weak acid.

Kb = ionization (or dissociation) constant of a weak base.

Kh = hydrolysis constant.

Kf = formation constant (mostly use for complex).

Kinst. = instability constant of complex ion.

Ion product constant for water (Kw) :

Aqueous solutions contains small amount of hydronium $[H_3O^+]$ and hydroxide

$[OH^-]$ ions as a consequence of the dissociation reaction :

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad \text{or} \quad \underset{\text{(acid)}}{H_2O} + \underset{\text{(base)}}{H_2O} \rightleftharpoons H_3O^+ + OH^-$$

H_2O acid gives H^+ to H_2O base to produce H_3O^+ .

$$K = \frac{[H3O+][OH-]}{[H2O]2}$$

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

$$Kw = [H_3O^+][OH^-] = 1x10^{-14}\ mol^2 / L^2$$

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K_w increase with the increase of temperature, and it decrease with decreasing of temperature.

K_w is used only for water and it applicated only for reversible reaction.

EX. : Calculate hydronium and hydroxide ion conc. of pure water at 25C° and 100C° ?

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

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

Subsititution into equation (2-10) gives :

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

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

At 25C° $[H_3O^+] = [OH^-] = \sqrt{1.01x10-14} = 1.01x10^{-7}$

At 100 C° $[H_3O^+] = [OH^-] = \sqrt{49x10-14} = 7.0x10^{-7}$

⇒ Calculating Equilibrium Concentrations

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

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 $[Br_2]= 2.3x10^{-3}$M,$[Cl_2] = 1.2 \times 10^{-2}$M, $[BrCl] = 1.4 \times 10^{-2}$ M. Write the equilibrium expression and calculate Kc for this reaction.

Solution:

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

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

Example 2\\ 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

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

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 3\\ A closed system initially containing 1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2 at 448℃ is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate K_c at 448℃ for the reaction taking place, which is

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

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
Equilibrium			1.87×10^{-3}

[HI] Increases by 1.87×10^{-3} *M*

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
Equilibrium			1.87×10^{-3}

Stoichiometry tells us $[H_2]$ and $[I_2]$ decrease by half as much.

	$[H_2]$, *M*	$[I_2]$, *M*	[HI], *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
Equilibrium			1.87×10^{-3}

Calculate the equilibrium concentrations of all three compounds...

	$[H_2]$, *M*	$[I_2]$, *M*	$[HI]$, *M*
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
Equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} = 51$$