Chapter 7

Equilibrium

RELATIONSHIP BETWEEN K_p AND K_c

$K_p = K_c(RT)^{\Delta n_g}$

where, $\Delta n_g = n_p - n_r$

= no of moles of gaseous product – no. of moles of gaseous reactant.

if $\Delta n_g = 0; K_p = K_c$; Example: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.

if $\Delta n_g > 0; K_p > K_c$; Example: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

if $\Delta n_g < 0; K_p < K_c$; Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Unit of K_p and K_c

Unit of $K_p = (atm)^{\Delta n_g}$

Unit of $K_c = (mol\ L^{-1})^{\Delta n_g}$

If $\Delta n_g = 0$, no unit of K_p and K_c

But now a days K_p and K_c are taken to be as unitless quantities.

Relation between degree of dissociation (α) and Vapour density

For equilibrium reaction

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

For a reaction $A \rightleftharpoons nB$

or $P \rightleftharpoons aA + bB + cC + ...$

where a + b + c .... = n

$$\boxed{\alpha = \frac{D-d}{(n-1)d}}$$

For (i) & (ii)

n = 2

$$\alpha = \frac{D}{d} - 1$$

D = Vapour density of the gas before dissociation = Molecular weight/2

d = Vapour density of equilibrium mixture

n = Total number of moles obtained after dissociation from 1 mole of dissociating molecule.

Relation between Equilibrium Constant (K) and Standard free energy Change (ΔG°)

$$\Delta G^\circ = -2.303RT \log K_c$$

$$\Delta G^\circ = -2.303\ RT \log K_p$$

LE-CHATELIER'S PRINCIPLE

It states that, if a system in equilibrium is disturbed by any external agency such as pressure, temperature, concentration etc. then equilibrium will get shifted to counter balance the effect of that disturbance.

Factors affecting Equilibrium

(1) Concentration

Addition of any reactant or removal of products leads to forward reaction or vice-versa.

(2) Temperature

In an endothermic reaction, $(\Delta H = +ve)$ increase in temperature favours the forward reaction, while decrease in temperature favours backward reaction.

For exothermic reaction, $(\Delta H = -ve)$ increase in temperature favours backward reaction, while decrease in temperature favours forward reaction.

(3) Pressure

Effect of pressure is mainly applicable to gaseous reactions, since liquids & solids are incompressible in nature.

If $\Delta n_g = 0$ pressure has no effect on equilibrium constant.

$\Delta n_g > 0$ then on increasing pressure, equilibrium will get shifted in the backward direction.

$\Delta n_g < 0$ then on increasing pressure, equilibrium will shift towards forward direction.

(4) Catalyst

A catalyst has no effect on state of equilibrium but it enables the state of equilibrium to reach very quickly.

(5) Inert gas

The introduction of inert gas to any equilibrium is visualized under the condition of constant volume and constant pressure.

(a) At constant volume

If $\Delta n_g = 0$, $\Delta n_g > 0$, $\Delta n_g < 0$ } no effect on equilibrium on addition of inert gas

(b) At constant pressure

If $\Delta n_g = 0$ no effect on equilibrium

Equilibrium will get shifted in that direction where no. of moles are more.

if $\Delta n_g > 0$ } In forward direction

$\Delta n_g < 0$ } In backward direction

IONIC EQUILIBRIUM

Dissociation of weak acids or weak bases and Ostwald's dilution law

When weak acid or weak base is dissolved in aqueous medium equilibrium exists between dissociated ions and undissociated molecules.

	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	+	H^+
Initially	C		0		0
At equilibrium	C(1-α)		Cα		Cα

where, α is the degree of dissociation.

$$\therefore \quad K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = C\alpha^2 \quad [\text{If } \alpha << 1]$$

$$\boxed{\alpha = \sqrt{\frac{K_a}{C}}} \text{ or } \boxed{\alpha = \sqrt{K_a \times V}} \text{ and } \boxed{[H^+] = C\alpha = C.\sqrt{\frac{K_a}{C}} = \sqrt{K_a C}}$$

Here V is the volume in litre containing 1 mole of electrolyte.

Similarly for weak base,

$$\boxed{\alpha = \sqrt{\frac{K_b}{C}}} \text{ or } \boxed{\alpha = \sqrt{K_b x\ V}} \text{ and } \boxed{[OH^-] = C\alpha = C.\sqrt{\frac{K_b}{C}} = \sqrt{K_b.C}}$$

Here V is the volume in litre containing 1 mole of electrolyte.

BUFFER SOLUTIONS

Types of Buffer Solutions

Acidic buffer : A mixture of weak acid and its conjugated base form acidic buffer. *e.g.*,

$CH_3COOH + CH_3COONa$

$HCOOH + HCOONa$

$C_6H_5COOH + C_6H_5COONa$

$$\boxed{pH = pK_a + \log \frac{[Salt]}{[Acid]}}$$

Basic buffer : It is a mixture of weak base and its conjugate acid.

Ex. (1) $NH_4OH + NH_4Cl$

(2) $Cu(OH)_2 + CuCl_2$

(3) $Mg(OH)_2 + MgSO_4$

$$\boxed{pOH = pK_b + \log\frac{[Salt]}{[Base]}}$$

$$\therefore \quad pH = 14 - pOH = 14 - \left(pK_b + \log\frac{[Salt]}{[Base]}\right)$$

$$pH = pK_w - \left(pK_b + \log\frac{[Salt]}{[Base]}\right)$$

SALT HYDROLYSIS

Consider the salt BA, which on hydrolysis will give acid and base inside the aqueous solution.

$BA + H_2O \rightleftharpoons BOH + HA$

(a) Salt made up of strong acid, strong base will not hydrolyse it will simply ionise. And pH of aqueous solution will be neutral. The pH of aqueous solution is independent with dilution *i.e.*, pH = 7. *e.g.*, NaCl, Na_2SO_4.

(b) Salt made up strong acid and weak base will hydrolyse, *e.g.*, NH_4Cl.

$$\boxed{K_h = \frac{K_w}{K_b}} \qquad pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

(c) Salt made up of weak acid and strong base, *e.g.*, CH_3COONa.

$$\boxed{K_h = \frac{K_w}{K_a}} \qquad pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

(d) Salt made up of weak acid and weak base. The pH and h of these salt solutions depend on K_a and K_b but independent with concentration, *e.g.*, CH_3COONH_4.

$$\boxed{K_h = \frac{K_w}{K_a.K_b}} \qquad pH = \frac{1}{2}[pK_w - pK_b + pK_a]$$

Note : $K_h = Ch^2$, $h = \sqrt{\frac{K_h}{C}}$, *where h = degree of hydrolysis.*

SOLUBILITY PRODUCT

When a sparingly soluble salt is dissolved in water, it forms saturated solution but concentration of salt is very low. Therefore in saturated solution of such electrolytes, solid electrolyte is in equilibrium with the ions as represented below:

$AgCl \rightleftharpoons Ag^+ + Cl^-$

Applying Law of chemical equilibrium

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

$$K[AgCl] = [Ag^+][Cl^-]$$

$$K_{sp} = [Ag^+][Cl^-]$$

where K_{sp} is a constant known as solubility product. It remains constant at constant temperature for a given salt and defined as the product of ionic concentration of a sparingly soluble electrolyte in a saturated solution.

if K_{sp} = I.P. (Ionic product) then solution is said to be saturated

if K_{sp} > I.P. then solution is said to be unsaturated

if K_{sp} < I.P. then solution is said to be supersaturated (Condition for precipitation)

Relation between Solubility and Solubility Product

For binary electrolyte; (for AB type salt)

$K_{sp} = S^2$ (AgCl, AgBr)

for ternary electrolyte; (for AB_2 or A_2B type salt)

$K_{sp} = 4S^3$ (CaF_2, $BaCl_2$)

for Quarternary Electrolyte; (for AB_3 or A_3B type salt)

$K_{sp} = 27S^4$

Solubility in presence of common ion

e.g. AgCl(s) is dissolve in xM Ag NO_3

$S = K_{sp} / x$

$\therefore$ $x >> S$ and $x + S \approx x$

$$AgNO_3 \longrightarrow \underset{x}{Ag^+} + \underset{x}{NO_3^-}$$

$$AgCl(s) \rightleftharpoons \underset{(S+x)}{Ag^+}(aq) + \underset{(S)}{Cl^-}(aq)$$

$[Ag^+]_{Total} = (x + S)$

$K_{sp} = (x + S)\, S$

In general due to common ion effect solubility of salt decreases.

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