CHEMICAL AND IONIC EQUILIBRIUM

Nature of Equilibrium

- Reactions which never go to completion and travel back-forth are said to be at equilibrium.
- Catalyst cannot change the direction of reaction
- Eqm is affected by Conc., P, T, V etc.

For a reaction, $\quad mA + nB \rightleftharpoons pC + qD$

$$k_f = [C]^p[D]^q \text{ and } k_b = [A]^m[B]^n$$

k = rate constant of forward reaction

k = rate of backward reaction

At Equilibrium, $k_f = k_b$ and $k_f / k_b = K_{eq}$

$^f_b \, K_c = \dfrac{[C]^p[D]^q}{[A]^m[B]^n}$	[ ] = represents concentration
$K_p = \dfrac{(p_C)^p(p_D)^q}{(p_A)^m(p_B)^n}$	p = partial Pressure also, $p = x \times P_T$

A ↔ B

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Relation between K_c, K_p, K_x

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

Case I : $n_p > n_r$; $\Delta n_g > 0$; $K_p > K_c$

Case II : $n_p < n_r$; $\Delta n_g < 0$; $K_p < K_c$

Case III : $n_p = n_r$; $\Delta n_g = 0$; $K_p = K_c$

K also confirms the stability of Reactants and Products

K↑ = Products Stable	K↓ = Reactants Stable

Factors Affecting K

- **Temperature (According to Van't Hoff equation)**

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H°}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{(Here } T_2 > T_1\text{)}$$

$\Delta H = +ve$ (Endothermic); $K_2 > K_1$

$\Delta H = -ve$ (Exothermic) ; $K_1 > K_2$

- **Stoichiometry of a reaction and representation**

For a reaction $aA + bB \rightleftharpoons cC + dD$, Eq. Constant K_1

1. Multiply reaction by 2 : K_1^2
2. Divide Reaction by 2 : $K_1^{1/2}$
3. Reverse the reaction : $1/K_1$
4. Add Equation with Eq. constant $K_2 = K_1.K_2$
5. Subtract Equation with Eq. constant $K_2 = K_1/K_2$

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Reaction Quotient

For a reaction $aA + bB \rightleftharpoons cC + dD$, Eqm Constant : K

At a stage other than eqm.

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

Q > K : Form Reactants
Q < K : Form Products
Q = K : Equilibrium

Degree of Dissociation ($0 < \alpha < 1$)

Fraction of initial molecules that are converted at eqm.

Case I :	aA	$\rightleftharpoons$	bB	If Initial moles = 2
n (Eq.)	2-ax		bx	Degree of diss. $\alpha = ax/2$

Case II :	aA	+	bB	$\rightleftharpoons$	cC	+	dD	If Initial A=3 ; B=2
n (Eq.)	3-ax		2-bx		cx		dx	DOD (α_A) = ax/3

Relation between Vapour Density and α

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

D = Vapour Density of Reactant
d = Vapour Density of Eqm. Mixture
α = degree of dissociation

- $n \neq 1$
- It is the sum of stoichiometric coefficients of the product side
- eg: $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$

  Here, n = 1/2 + 3/2 = 2

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Simultaneous Equilibrium

- If, there are two or more eqm. existing simultaneously involving one or more than one common species.
- Then, conc. of common species = total concentration in all eqm.

Relation between Standard Gibbs Free Energy and K

$$\Delta G° = -2.303nRT \log K = -nRT \ln K$$

| $\Delta G° < 0$	K>1	Spontaneous Reaction
$\Delta G° > 0$	K<1	Non-Spontaneous Reaction
$\Delta G° = 0$	K=0	Equilibrium

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Le-Chatlier's Priniciple

When a simple system in equilibrium is subjected to a change in Conc., T, V, or P.
(1) the system changes to a new equilibrium
(2) this change partly counteracts the applied change.

Concentration	↑ Reactants - **Forward** Reaction ↑ Products - **Backward** Reaction
Temperature	Endothermic : ↑Temp - **Forward** Exothermic : ↑Temp - **Backward**
Catalyst	BORRINGGG....**NO EFFECT**
Pressure	↑ Pressure : **Towards Lower moles** ↓ Pressure : **Towards Higher moles**
Inert Gas	At Constant P, **Towards Higher Moles** At Constant V, **NO Effect**
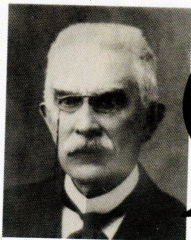
Are you Getting my point?

Henry Louis Le Chatelier

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Electrolytes and Non Electrolytes

Electrolytes - Which dissociate into ions

Strong Elec. ($\alpha = 1$)	• All strong acids and salts (HCl, HNO_3) etc. • All Alkali metal hydroxides and $Ba(OH)_2$
Weak Elec. ($0 < \alpha < 1$)	• HNO_2, H_2SO_3, $HClO$, All oxy acids of P, All organic acids, HCN, H_3BO_3, H_2CO_3 etc. • All Alkaline hydroxides except $Ba(OH)_2$, All organic bases, D-series hydroxides.

Theories of acids and bases

Theory	Arrhenius	Bronsted	Lewis
ACIDS	Donates H^+	Donates H^+	Lone Pair Acceptor
BASES	Donates OH^-	Accepts H^+	Lone Pair Donor

NOTE

• Strong Acid → H^+ + Weak Conjugate base **and**
• Strong Base + H^+ → Weak Conjugate base **VICE VERSA**

• Amphiprotic acids are H^+ donor and acceptor, H_2CO_3

Ionic product of water

At 25°C, $K_w = [H^+][OH^-] = 10^{-14}$
For Pure water, $[H^+] = [OH^-] = 10^{-7}$

K_w increases with increase in temperature.

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pH Calculation

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

At 25°C, $pH + pOH = pK_w$

Case I : Strong acids/bases with $[H^+] \geq 10^{-6}$

- Directly take the log of concentration of H^+

Case II : Strong acids/bases with $[H^+] < 10^{-6}$

$$pH = -\log(H^+_{acid} + H^+_{water}) \ \textit{Here}, \ H^+_{water} = 10^{-7}$$

Case III : Mixture of Strong acids/bases

Two Strong Acids	**Two Strong Bases**
$[H^+] = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$	$[OH^-] = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$

Case IV : Case of Weak mono acids and bases

For a weak acid, $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

More the value of K_a, Stronger is the acid

$$1-\alpha \approx \ \ \alpha = \sqrt{\frac{K_a}{c}}$$

α = Degree of Dissociation
c = Concentration of HA

$$pH = -\log_{10}\sqrt{K_a c} = \frac{1}{2}(pK_a - \log_{10} c)$$

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Case V : Weak Poly basic acid/ Weak poly acidic base	
H_3PO_4 will have three dissociation constants : Ka_1, Ka_2 & Ka_3. The calculation of pH is dependent upon,	$pH = \dfrac{1}{2}[pKa_1 - \log c]$ not dependent upon the other constants

Case VI : Mixture of two weak acids or two weak bases	
$[H^+] = \sqrt{Ka_1 c_1 + Ka_2 c_2}$	c_1 & c_2 conc. after mixing

Case VIII : pH of Amphiprotic acids	
	$pH = \dfrac{(pKa_1 + pKa_2)}{2}$

Salt Hydrolysis

Hydrolysis Constant, K_H	pH of solution

Weak Acid - Strong Base (pH > 7)

$K_h = \dfrac{ch^2}{1-h} = \dfrac{K_w}{K_b}$	$pH = \dfrac{1}{2}[pK_w - (pK_b + \log c)]$

Weak Base - Strong Acid (pH < 7)

$K_h = \dfrac{ch^2}{1-h} = \dfrac{K_w}{K_a}$	$pH = \dfrac{1}{2}[pK_w + (pK_a + \log c)]$

Weak Base - Weak Acid (pH depends on Ka and Kb)

$K_h = \dfrac{h^2}{(1-h)^2} = \dfrac{K_w}{K_a . K_b}$	$pH = \dfrac{1}{2}[pK_w + (pK_a - pK_b)]$

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Buffer Solution

Acidic Buffer	Basic Buffer
WA + Salt of WA&SB	WB + Salt of WB&SA
• H_2CO_3 + $NaHCO_3$ • HNO_2 + $NaNO_2$ • CH_3COOH + CH_3COONa	• NH_4OH + NH_4Cl • $PhNH_2$ + $PhNH_3^+Cl^-$ • CH_3NH_2 + $CHNH_3^+Cl^-$

Henderson Equation

$$pH = pK_a + \log_{10} \frac{[Salt]}{[Acid]} \text{ or } \frac{[Conjugated Base]}{[Acid]}$$

$$pOH = pK_b + \log_{10} \frac{[Salt]}{[Base]} \text{ or } \frac{[Conjugated Acid]}{[Base]}$$

Buffer Capacity
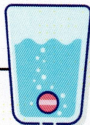
Number of moles of strong acid/base per L of Soln.

Solubility Product (Ksp)

For a salt A_xB_y

$$s = \left[\frac{(K_{sp})}{x^x \cdot y^y} \right]^{\frac{1}{x+y}}$$

In case of Common ion, the Solubility decreases as reaction moves backwards. E.g. AgCl in Cl^-

$$s = \frac{K_{sp}{}^{AgCl}}{[Cl^-]}$$

• In case of complex formation, solubility of salt is maximum.

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Ionic Product of salt

For a salt A_xB_y

$$K_{IP} = [A^{y+}]^x[B^{x-}]^y$$

$K_{IP} > K_{sp}$ Ppt occurs

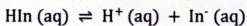$K_{IP} < K_{sp}$ Unsaturated soln
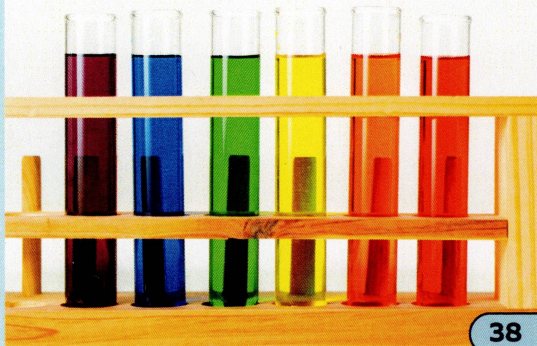
$K_{IP} = K_{sp}$ Saturated soln

Indicator Theory

Indicators are either weak acids or weak bases and when dissolved in water, their dissociated form acquires a colour different from that of the undissociated form.

The human eye can detect the change in colour if the ratio of the two forms of indicator ranges between 0.1 to 10.

$$HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \text{ or } \frac{[HIn]}{[In^-]} = \frac{[H^+]}{K_{In}}$$

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