MIND MAP

Ionic Equilibrium

Electrolytes

Strong Electrolyte

Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.
For strong electrolyte : $\alpha = 1$
Eg.-H_2SO_4, HCl, KOH, NaOH, $Ba(OH)_2$,

Weak Electrolytes

Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of α is less than one.($\alpha << 1$)
Eg.-HCN,CH3COOH,HCOOH, H_2CO_3,NH_4OH,$Cu(OH)_2$,$Zn(OH)_2$

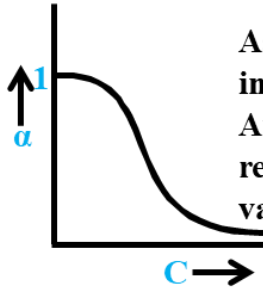
Degree of Dissociation / Ionisation

The degree of dissociation (α) of an electrolyte is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initally}}$$

Ostwald's Dilution Law (For Weak Electrolytes)

$$\alpha = \sqrt{\frac{K_{diss}}{C}} \qquad \alpha \propto \frac{1}{\text{concentration}}$$



As concentration increases, α decreases
At infinite dilution α reaches its maximum value, unity.

Common Ion Effect

The degree of dissociation of a weak electrolyte is suppressed by the addition of another electrolyte(strong) containing common ion. This is referred to as common ion effect

Acids and Bases

Arrhenius Acid

Substances which give H^+ ion on dissolving in water (H^+ donor)
Ex. HNO_3, $HClO_4$, HCl, H_2SO_4, H_3PO_4 etc.

Arrhenius Base

Any substance which releases OH– (hydroxyl) ion in water (OH– ion donor)
Ex. NaOH , $Ca(OH)_2$

Strength of Acid or Base

Strength of Acid or Base depends on the extent of its ionisation. Hence equilibrium constant Ka or Kb respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Bronsted Lowery Concept

Conjugate acid - base concept, Protonic concept

Acid: substances which donate H^+ are Bronsted Lowery acids (H^+ donor)

Base: substances which accept H^+ are Bronsted Lowery bases (H^+ acceptor)

Lewis Concept (Electronic Concept)

A Lewis acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

Acid → e^- pair acceptor

Ex.- $BF_3, AlCl_3, H^+, Fe^{2+}, Na^+, SF_4, PF_3$

A lewis base is any molecule/ion which has a lone pair of electrons which can be donated.

Base → electron pair donor

Ex. $NH_3, PH_3, H_2O, CH_3OH, OH^-, H^-, NH_2^-$

pH scale

$pH = -\log_{10} a_{H^+}$ (where a_{H^+} is the activity of H^+ ions)

pOH scale

$pOH = -\log_{10} a_{OH^-} = -\log_{10}[OH^-]$

For a weak monoprotic acid HA

$pKa = -\log_{10} ka$

For a weak monoprotic base MOH

$pKb = -\log_{10} kb$

Molar Concentration / Molarity of Water

Molarity = No. of moles / litre

= 55.55 M (density = 1 g/cc)

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Ionic Product of Water

$H_2O \rightleftharpoons H^+ + OH^-$

So, ionic product of water

$K_w = [H^+][OH^-] = 10^{-14}$ at 25° (exp.)

Dissociation of water is endothermic, so on increasing temperature K_w increases.

K_w increases with increase in temperature.

$pH = -\log[H^+] = 7$

for water at 25°C (experimental)

$pH < 7 \Rightarrow$ acidic

$pH > 7 \Rightarrow$ Basic } at 25 °C

$pH = 7 \Rightarrow$ neutral

Ionic product of water is always a constant.

Dissociation constants of pure water

$H_2O \rightleftharpoons H^+ + OH^-$

$Ka = Kb = 1.8 \times 10^{-16}$

Relation between conjugate acid base dissociation constants

$pK_a + pK_b = pk_w = 14$

only for conjugate acid–base pair

pH Calculation of Different Type of Solutions

(a) Strong acid solution

If concentration of H^+ ions is $\geq 10^{-6}$M

In this case H^+ ions coming from water can be neglected.

(ii) If concentration is less than 10^{-6}M. In this case H^+ ions coming from water cannot be neglected.

So $[H^+]$ = H^+ from acid + H^+ ions coming from water in presence of this strong acid

(b) Strong base solution

If concentration of OH^- ions is $\geq 10^{-6}$M

In this case OH^- ions coming from water can be neglected.

If concentration of OH^- ions is $< 10^{-6}$M

In this case OH^- ions coming from water can not be neglected.

(c) pH of mixture of two strong acids

Number of H^+ ions from I-solution = N_1V_1

Number of H^+ ions from II-solution = N_2V_2

If final normality is N and final volume is V, then

$NV = N_1V_1 + N_2V_2$ $[H^+] = \dfrac{N_1V_1 + N_2V_2}{V_1 + V_2}$

where $N = M \times n$ (n = Basicity of acid)

(d) pH of mixture of two strong bases

Similarily,

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

$$[H+] = \frac{10^{-14}}{[OH^-]}$$

where $N = M \times n$ (n = Basicity of acid)

(e) pH of mixture of a strong acid and a strong base

The solution will be acidic or basic depending on which component has been taken in excess.

$$[H^+]/[OH^-] = \frac{|N_AV_A - N_BV_B|}{V_A + V_B}$$

(f) pH of a weak acid (Monoprotic) Solution

$$pH = \frac{1}{2}(pKa - \log C)$$

On increasing the dilution

$\Rightarrow C\downarrow = \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

(g) pH of a mixture of weak acid (monoprotic) and a strong acid solution

$HB \rightarrow C_1$

HB	$\rightleftharpoons$	H^+	$+$	B^-
C_2		C_1		0
$C_2(1-\alpha)$		$C_2\alpha + C_1$		$C_2\alpha$

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Ionic Equilibrium

$$K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1-\alpha)} \quad (\alpha << 1)$$

(h) pH of a mixture of two weak acid (both monoprotic) solution

$\Rightarrow C_w$

$$[H^+] = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$$

Hydrolysis of Salts

Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of H+ and OH– ions of water.

$Salt + H_2O \rightleftharpoons Acid + Base$

Types of Salt Hydrolysis

(1) Hydrolysis of [SA – SB] type salt

No Hydrolyis.

(ii) Hydrolysis of strong acid - weak base [SA - WB] type salt

(1) $K_h = \frac{K_w}{K_b}$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \times C}}$

(3) $[H^+] = Ch = \sqrt{\frac{K_w \times C}{K_b}}$

(4) $pH = -\log[H^+]$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

Hydrolysis of [WA – SB] Type Salt

Ex. KCN, NaCN, K_2CO_3, $BaCO_3$, K_3PO_4

(1) $K_h = \frac{K_w}{K_a}$

(2) $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \times C}}$

(3) $[OH^-] = Ch = \sqrt{\frac{K_w \times C}{K_a}}$

(4) $[H^+] = \sqrt{\frac{K_w \times K_a}{C}}$

(5) $pH = -\log[H^+]$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

Hydrolysis of (WA - WB) Type Salt

Ex.

NH_4CN, $CaCO_3$, $(NH_4)_2CO_3$,

$NH_4CN + H_2O \rightleftharpoons NH_4OH + HCN$

(1) $K_h = \dfrac{K_w}{K_a \times K_b}$

(2) $h = \sqrt{K_h} = \sqrt{\dfrac{K_w}{K_a \times K_b}}$

(3) $[H+] = \sqrt{\dfrac{K_w \times K_a}{K_b}} = Ka.h$

(4) $pH = -\log [H^+]$

$pH = 7 + \frac{1}{2}[pK_a - pKb]$

Hydrolysis of Amphiprotic Anion

$NaHCO_3$, NaHS, etc., can undergo ionisation to form H+ ion and can undergo hydrolysis to form OH^-.

$$pH = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right)$$

Buffer Solutions

A solution that resists change in pH value upon addition of small amount of strong acid or base or when solution is diluted is called buffer solution.

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Ionic Equilibrium

(a) Acidic buffer solution

An acidic buffer solution consists of solution of a weak acid and its salt with strong base.

$HCN + KCN$, $(H_2CO_3 + NaHCO_3)$

$\longrightarrow$ blood (Weakly ionised)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$

(Highly ionised)

pH Of a acidic buffer solution (Handerson Equation)

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$[A^-]$ = Initial concentration of salt as it is mainly coming from salt.

[HA] = Initial concentration of the acid.

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

(B) Basic Buffer Solution

Basic buffer solution consists of a mixture of a weak base and its salt with strong acid.

pH of Basic Buffer Solution

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

$\Rightarrow$ $pH = 14 - pOH$

pOH range

A solution can act as buffer solution only if ratio of concentration of salt to base is from 0.1 to 10.

NH_4OH :	NH_4Cl	
1	10	$pOH = pK_b + 1$
10	1	$pOH = pK_b - 1$

So pOH range is pKb $\pm$ 1

pH range

A solution can act as buffer solution only if ratio of concentration of salt to acid is from 0.1 to 10.

CH3COOH:	CHCOONa	
1	10	$pH = pK_a + 1$
10	1	$pH = pK_a - 1$

So pH range is pKa $\pm$ 1

Buffer Capacity

Moles of H+ or OH- ions that must be added to 1 liter of a buffer solution to change its pH by 1 unit.

Higher the Buffer capacity, better is the buffer solution.

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Ionic Equilibrium

Indicators

An indicator is a substance which changes its colour at the end point or neutral point of the acid-base titration i.e. the substance which is used to indicate neutral point of acid-base titration are called indicators.

At end point $N_1V_1 = N_2V_2$

S.No	Indicators	pH range	Colour in acidic med.	Colour in basic med.
1.	Methyl orange	3.1 to 4.4	red	Yellow
2.	Methyl red	4.2 to 6.3	red	Yellow
3.	Phenol red	6.8 to 8.4	Yellow	red
4.	Phenolphthalie	8.3 to 10	colourless	red

Solubility

At constant temperature the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of solution.

$$s(M) = \frac{\text{Max. number of moles of solute}}{\text{Volume of solution (L)}}$$

Solubility Product(Ksp)

- General form

$A_xB_y(s) \rightleftharpoons xA^{+y}(aq) + yB^{-x}(aq)$

$$K_{sp} = x^x . y^y . s^{(x+y)}$$

Condition Of Ionic Product (IP Or Qsp)

- IP = $[Ag^+][Cl^-]$(at all concentration) and K_{sp}= $[Ag^+][Cl^-]$(at equilibrium)

If

(i) IP < K_{sp} : The solution is unsaturated and precipitation will not occur.

(ii) IP = K_{sp} : The solution is saturated and solubility equilibrium exists.

(iii) IP > K_{sp} : The solution is supersaturated and hence precipitation of the compound will occur.

A salt is precipitated when its ionic product exceeds the solubility product of the salt.

Common Ion Effect On Solubility

Simultaneous Solubility

- When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the solution.

Selective Precipitation

When the Ksp values differ then one of the salt can be selectively precipitated.

Effect on Solubility because of Complex Formation

Solubility of AgCl in aqueous NH3 is roughly 10,000 its solubility in water as shown in problem below

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$