# Volumetric analysis

- Acidimetry – determination of strength of Alkali with help of Standard sol$^{n}$ (known) of acid.
- Neutralization → same value of eqv. amt. of acid & base reacts. (not always pH = 7)

# Selection of indicator { MeOH → 3.1 - 4.4 (pH range
Permanganometry → KMnO$_4$ Hph → 8.2 - 10 ; Litmus (5-5-8) }
Iodometry → Starch

- SA & SB → MeOH; Hph or Litmus (4-10)
- SA & WB → MeOH (3-8)
- WA & SB → Hph (8.6-11)
- WA & WB → None.

Same Normality of acid is neutralized by alkali having same Vol.

No. of gm-eqv. = $\frac{\text{Given mass}}{\text{Eqv. wt.}}$

20ml 5N $H_2SO_4$ =
10ml 10N $H_2SO_4$ =
5ml 20N $H_2SO_4$ =
5ml 10M $H_2SO_4$

# Equivalent weight

- **Element** : (i) If there is H, compare with 1

(ii) $E_{element} = \frac{\text{Atomic wt.}}{\text{Valency.}}$ O → 8, Cl → 35.5

$E = \frac{A}{V}$

- **Acid**:

Eq. wt. of acid = $\frac{\text{Mol wt. of Acid}}{\text{Basicity (No. of replaceable hydrogen present in 1 molecule of acid)}}$

H attached with O → Depends on rxn.

* $H_3PO_4$ (M) → Eq. wt. = $\frac{M}{3}$
* $H_3PO_3$ (M) → Eq. wt. = $\frac{M}{2}$
* $H_3PO_2$ (M) → Eq. wt. = $\frac{M}{1}$ = M

* $H_3BO_3$ (M) → Eq. wt → $\frac{M}{1}$ = M

☆ Normality Volume आउँ आउ (can exchange numerically)

- **Base**:

Eq. wt. of Base = $\frac{\text{Mol. wt. of Base}}{\text{Acidity (No. of gram eqv. wt. of acid required for 1 mole of Base)}}$

**Trick**

Oxide → Divide with 2 × no. of oxygen atoms per molecule.

Hydroxide → Divide with no. of OH$^-$ ions per molecule.

- **Salt**:

Eq. wt. of salt = $\frac{\text{Mol. wt. of salt}}{\text{Total charge of cation or anion per molecule}}$

- Eq. wt. of radical = $\frac{\text{Mass of radical}}{\text{Charge of radical.}}$
- Eq. wt. of oxidant or Reductant = $\frac{\text{Mol wt. of oxidant (or Reductant)}}{\text{Change in total O.N. per molecule (OR, total no. of electrons lost or gained per molecule)}}$

Eg. (i) KMnO$_4$ (M) → acidic → M/5 ($MnO_3$)
→ Basic → M/1 ($MnO_4^{--}$)
→ Neutral → M/3 ($MnO_2$)

(ii) $K_2Cr_2O_7$ (M) → all medium → M/6 ($Cr_2O_3$)

Reaction always occurs in proportion to their gm. eqv.

# Concentration terms

① % (w/V) = $\frac{\text{wt. of solute (in g)}}{\text{Vol. of soln (in ml)}} \times 100$ { 4 % NaOH soln by v/v; 4% NaOH soln (w/v); 4% of NaOH soln

② % (w/w) = $\frac{\text{wt. of solute (in g)}}{\text{Vol. of soln (in g)}} \times 100$ { 4% NaOH soln by wt; 4% NaOH soln (w/w); 4% NaOH soln (given Sp. gravity)

③ G/L = $\frac{\text{wt. of solute (in g)}}{\text{Vol. of soln (in L)}}$

④ Normality (N) = $\frac{\text{Amt. of substance dissolved in gm-eqv. (No. of gm-eqv. of solute)}}{\text{Vol. of soln in Litre}}$

$= \frac{\text{Amt. of substance dissolved (in gm) \{w\}}}{\text{Eqv. wt. of substance (E)}}$ / $\frac{\text{Vol. of soln in ml (V)}}{1000}$

$N = \frac{(w/v)\% \times 10}{\text{eq. wt.}}$

$N = \frac{(w/w)\% \times \text{sp. gravity} \times 10}{\text{eq. wt.}}$

$\Rightarrow N = \frac{w \times 1000}{E \times V}$

Normality factor (f) = $\frac{\text{wt. taken}}{\text{wt. to be taken}}$

⑤ Molarity (M) = $\frac{\text{Amt. of substance dissolved in mole}}{\text{Vol. of soln in Litre}}$

$M = \frac{(w/v)\% \times 10}{\text{Mol. wt.}}$

No. of moles = (Vol. of soln in l) × M

$M = \frac{w}{M_w} \times \frac{1000}{V \text{ (in ml)}}$

$N = \text{X-factor} \times M$ (X-factor: Acidity, Basicity)

⑥ Molality (m) = $\frac{\text{Amt. of substance dissolved in mole}}{\text{wt. of solvent in kg.}}$

$m = \frac{w}{M_w} \times \frac{1000}{W_{solvent} \text{ (in g)}}$

$M = \frac{(w/w)\% \times \text{sp. gravity} \times 10}{\text{mol. wt.}}$

⑦ Mole fraction (x)

$X_A = \frac{n_A}{N_B + n_A}$ $\quad X_B = \frac{N_B}{N_B + n_A}$

$X_A$ = Mole fraction of solute
$x_B$ = Mole fraction of solvent
$n_A$ = no. of mole of solute
$n_B$ = no. of mole of solvent

$X_{solution} = X_A + X_B = 1$

$\frac{w}{E_w} = \frac{V}{E_V}$ Lt.

# Notes

(i) For complete Rxn b/w ① & ②: $N_1 V_1 = N_2 V_2$

(ii) Strength of mixture:

→ $V_m N_m = V_1 N_1 + V_2 N_2 + V_3 N_3$ { When all soln are of same type (i.e. acid or alkali)

→ $V_m N_m = \underbrace{V_1 N_1 + V_2 N_2}_{\text{Acids}} - \underbrace{\{V_1' N_1' + V_2' N_2'\}}_{\text{Alkalis}}$ { If $(V_1 N_1 + V_2 V_2) > (V_1' N_1' + V_2' N_2')$

$V_m = V_1 + V_2 + V_1' + V_2'$

(iii) Concentration $\propto \frac{1}{\text{Dilution (volume)}}$

(iv) Normality × Eq. wt = Molarity × Mol. wt. $\Rightarrow N E = M M_w$

# Ionic product of water ($K_w$) = $[H^+][OH^-] = 10^{-14}$ {At 25°C}

- Temp ↑ ⇒ $K_w$ ↑
- In pure water, $[H^+] = [OH^-]$
- $K_w$ ⇒ constant for given temp.
- In acidic soln, $[H^+] > [OH^-] \Rightarrow [H^+] > 10^{-7}$ M
  In Alkaline soln, $[H^+] < [OH^-] \Rightarrow [OH^+] < 10^{-7}$ M

& $[H^+] = [OH^-] = 10^{-7}$

$K_e = \frac{[H^+][OH^-]}{[H_2O]}$ → {Conc. of pure water at 25°C is 55.5 M i.e. 55.5 mol/litre}

# pH scale – Sorenson

- $pH = -\log_{10}[H^+]$ ⇒ $[H^+]$ → in M
  $[H^+] = 10^{-pH}$
- pH → Dimensionless
- At, 25°C; pH + pOH = 14
  For acid soln, pH < 7; For alkaline soln pH > 7
- For pure water, pH = pOH = 7

{$pH = -\log_{10}[H^+]$ ↓ in Normality for direct calculation}

**Caution!**
Unless mentioned, the given condition at NTP,
1 mole ≠ 22.4 Litre
In other condition,
18ml water = 18gm

# Ostwald's Dilution law [For weak electrolyte]

- For strong electrolyte, they dissociate completely into their ions on dilution.
- Weak electrolyte → only dissociates slightly into ions.
- HA → weak acid

$HA \rightleftharpoons H^+ + A^-$

Initial: 1 mole, 0, 0
eqm: $(1-\alpha)$ mole, $\alpha$ mole, $\alpha$ mole.

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{1-\alpha}{V}} = \frac{\alpha^2}{(1-\alpha)V} = \frac{\alpha^2 C}{1-\alpha}$ [$\alpha <<< 1$ for weak electrolyte]

For weak acid ⇒ $\boxed{K_a = \alpha^2 C}$ → Concentration of HA in mole/litre
$K_a$ → dissociation constant of acid

$\alpha = DOD = \frac{\text{Dissociated moles}}{\text{total moles}}$

HA → concentration C → 1 mole dissolved in V litre → ★ $C = \frac{1}{V}$ mole/Lit

$[H^+] = \frac{\alpha}{V} = \alpha C$

- $K_a$ ↑ ⇒ Acidic strength ↑
- $[H^+] = \sqrt{K_a \times C} = \alpha C$
- $pK_a = -\log K_a$ ; $pK_b = -\log K_b$
- $pK_a$ ↓ ⇒ Acidic strength ↑

{If $[H^+] < 10^{-7}$ in acidic solution, then $[H^+]$ of water i.e $10^{-7}$ is also taken to calculate pH. Similarly, for basic solution $[OH^-] < 10^{-7}$ the $[OH^-]$ of water is also taken to calculate pOH.}

# Solubility product

- For insoluble or slightly soluble ionic compound mixed in water (saturated)
- Eqm exists b/w undissolved solid & its ions. Dissociates slightly in water
- Eg. $BaSO_4(s) \rightleftharpoons BaSO_4(aq) \rightleftharpoons Ba^{++}(aq) + SO_4^{--}(aq)$

$K [BaSO_4]_s = [Ba^{++}_{aq}][SO_4^{--}_{aq}]$

$K_{sp}$ for $BaSO_4$ ⇒ solubility product

- Conc$^n$ of solid → constant

**Conjugate acid-base pair**
Acid $\xrightarrow{-H^+}$ conjugate base
Base $\xrightarrow{+H^+}$ Conj. Acid
differ by single proton ($H^+$)

- For ionic compound $A_x B_y$

Mol. Formula → $A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}$

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

Solubility → Amt. of substance dissolved in certain vol. of sol$^n$ to make the sol$^n$ saturated at given temp. (defined for all types of electrolyte)

- Solubility & solubility product ⇒ saturated solution.
- $K_{sp}$ → constant for given temp.
- Solubility ⇒ expressed in mole per Litre
- In mixture, $K_{sp}$ is constant for solubility changes.
- (IV) $K_{sp}$ → constant irrespective of other ions in the solution.
- $K_{sp}$ of salt ↑ ⇒ solubility in water ↑

# Ionic product (Q) → product of conc$^n$ of ions in sol$^n$

- $Q = K_{sp}$ ⇒ saturated sol$^n$ & no ppt
- $Q < K_{sp}$ ⇒ unsaturated sol$^n$ & no ppt.
- $Q > K_{sp}$ ⇒ supersaturated sol$^n$ & ppt occurs

- Q → variable & can be measured at any concentration (sat, unsat. or super sat)

# Common-ion effect.

↳ suppression of ionization of weak electrolyte in presence of strong electrolyte having common-ion.

↳ In common-ion effect, solubility differ but $K_{sp}$ remains same at given temp.

# Buffer solution

(I) Acidic Buffer :- weak acid + its salt obtained from strong base.

eg: $CH_3COOH + CH_3COONa$

(II) Basic Buffer :- weak base + its salt obtained from strong acid

eg: $NH_4OH + NH_4Cl$

- pH of Acid buffer = $pK_a + \log \frac{[Salt]}{[Acid]}$
- pOH of Basic buffer = $pK_b + \log \frac{[Salt]}{[Base]}$

# Salt hydrolysis

(I) salt of S.A. & S.B ⇒ No hydrolysis ⇒ aq. solution : Neutral

(II) salt of S.B & W.A ⇒ Anions of salt & $H^+$ of water combines ⇒ aq. solution : Basic
Eg: $CH_3COONa$, $NaCN$, $Na_2CO_3$ (Anionic hydrolysis)

(III) salt of S.A. & W.B ⇒ cation of salt & $OH^-$ of water combines ⇒ aq. solution : Acidic
Eg: $NH_4Cl$, $CuSO_4$, $FeCl_3$ (Cationic hydrolysis)

(IV) salt of W.A. & W.B ⇒ Both ions are strong and hydrolysed ⇒ aq. solution : Acidic or basic or neutral depending upon relative strength.

Eg (III) $NH_4Cl_{(aq)} \rightarrow NH_4^+_{(aq)} + Cl^-_{(aq)}$ → HCl

$NH_4^+ + OH^- \rightarrow NH_4OH$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ ; Being weak tries to remain undissociated

(weak electrolyte)

$HCl \rightarrow H^+ + Cl^-$

(S.E.) → remains in ionic form → $[H^+] > [OH^-]$

# Electrochemistry

$\Delta H$ = -ve, $\Delta G$ = -ve
$\Delta S$ = +ve → spa

## # Quantitative Aspect of Electrolysis:-

### 1st law:

The amount of substance deposited or the amount of gas liberated at the particular electrode during electrolysis is directly proportional to the quantity of charge (electricity) passed through the electrolyte solution

W → wt. (in g) deposited at cathode after electrolysis

i.e. $W \propto Q$

or, $W = ZQ$

or, $W = ZIt$

W → amount of substance deposited (in gram)

Z → constant: Electrochemical equivalent (ECE) ↳ mass of substance (in g) deposited by passing 1 C charge

I → current in Ampere

t → time for which current I is passed. in sec.

1 F = Charge on 1 mole of electrons.

1 Faraday (96500 Coulomb) charge deposits (or discharge or liberate) 1 gram equivalent of any substance.

1 mole electron ≡ 1 faraday ≡ 1 gm-eqv.

96500 coulomb deposits E g of substance

1 coulomb deposits $\frac{E}{96500}$ g of substance

E → Equivalent weight of a substance

$E = \frac{\text{Molecular mass}}{x}$

x = e⁻ transfer / charge change / valency factor

But, By definition of Z (ECE),

$Z = \frac{E}{96500}$

Unit of Z: gram coulomb$^{-1}$

Relation b/w ECE & chemical eqv. (E)

$Z \propto E$

($\frac{1}{96500}$ is constant)

For 2 substances 1 and 2,

$Z_1 \propto E_1$ & $Z_2 \propto E_2$

$\Rightarrow \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$

$W = \frac{EIt}{96500}$

∵ 1 mole of electron can deposit 1 gm. eqv. of substance.

* 1 mole electron (Charge) = $N_A \times 1.6 \times 10^{-19}$ C = 96500 C = 1 Faraday

$\rho = \frac{m(W)}{V}$

(W) $m = \rho \times V$

m → gram, ρ → gram/cm³, V → cm³

$V = A \times \theta$

A → Area (cross-section), θ → thickness of plating

Number of gram equivalent = $\frac{\text{Mass of solute in gram}}{\text{Equivalent wt. of solute}}$

1 mole → molar mass

1 gm equivalent → equivalent mass.

* Kohlrausch's law,

For infinite dilution,

$\lambda^\circ = \lambda^\circ_+ + \lambda^\circ_-$

$\lambda^\circ$ → equ. conductance of electrolyte

$\lambda^\circ_+$ → eqv. cond. of cation

$\lambda^\circ_-$ → of anion.

## 2nd law :- (same current / same charge) ⇒ Q same ⇒ It same ⇒ I (in series) & t same

When same quantity of electricity is passed through different electrolytic solution (connected in series), then the mass of substance deposited or liberated at the respective electrodes is directly proportional to its chemical equivalent or equivalent weight.

Mass of substance discharged (W) ∝ chemical equivalent (E)

In terms of Vol. at NTP

$$\frac{V_1}{Eq.\ Vol_1} = \frac{V_2}{Eq.\ Vol_2}$$

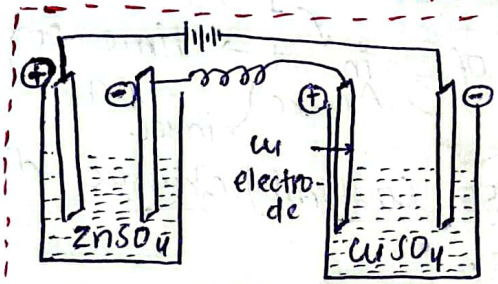
$W \propto E$

or $W = kE$ [k → proportionality constant]

or $\frac{W}{E} = k$ i.e. $\frac{\text{mass of substance deposited or liberated}}{\text{chemical equivalent of that substance}} = \text{constant}$

Accordingly,

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$$




$m_{Zn} = Z_{Zn} Q$ — (i) ($m_{Zn}$ → mass of Zn deposited)

$m_{Cu} = Z_{Cu} Q$ — (ii)

(i) ÷ (ii)

$$\frac{m_{Zn}}{m_{Cu}} = \frac{Z_{Zn}}{Z_{Cu}}$$

$$\frac{m_{Zn}}{m_{Cu}} = \frac{E_{Zn}/F}{E_{Cu}/F}$$

$m \propto Eq.wt.$ $\quad \frac{m_1}{m_2} = \frac{E_1}{E_2}$

$\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + \Delta nRT$

* Approx. atomic wt. × Sp. heat ≈ 6.4
* Specific conductance (K) = $\frac{1}{R} \cdot \frac{l}{A}$ ↳ siemens cm⁻¹
* Equivalent conductance ($\lambda$) = $\frac{l \times 1000}{R \cdot A \cdot N}$ ↳ siemens cm² equiv⁻¹
* Molar conductance ($\mu$) = $\frac{l \times 1000}{R A M}$ ↳ siemens cm² mol⁻¹

$l$ = length of sep. (cms)
$R$ = Resistance
$A$ = CSA of electrode (cm²)
$N$ = Normality of sol$^n$.
$M$ = Molarity of sol$^n$ (mol/l)

* $\lambda \times N = \mu \times M$
* $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
* $\Delta G = -nFE$ [n = no. of moles of e⁻ lost/gained; E → Emf of cell; F = 96500C]
* $\Delta G = -RT \ln K_{eq.}$
* Nerst eqⁿ, → $E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$ → Molar conc. of reduced species / Molar conc. of oxidised species. [Molar conc. of pure metal is arbitrarily taken as 1]

$\Delta G = \Delta G^\circ + RT \ln Q_{eq.}$ $\quad \Delta G = -RT \ln K_{eq.}$

1 mole electron = 1 faraday = 96500C → 1 gm. eqv. (deposited/liberated)

# Volume (deposited or liberated) at NTP = $\frac{It}{F}$ × Eq. Volume.

Eq. Volume → Vol. occupied by 1 gm. eqv. of of gas at NTP.

eg: (i) Eq. Vol. of $Cl_2$ = Vol. occupied by 35.5 gm $Cl_2$
i.e. Eq. vol. of $Cl_2$ = 11.2 Litre

(ii) Eq. Vol. of $O_2$ = Vol. occupied by 8 gm $O_2$ = 5.6 litre

(iii) Eq. Vol. of $H_2$ = Vol. occupied by 1 gm $H_2$ = 11.2 litre.

# Eq. wt. of $H_2O$ = 9.

# Efficiency of current ($\eta$) = $\frac{m \times F}{E \times I \times t} \times 100$

# No. of charge required to deposit,
1 mole of $M^{n+}$ = nF coulomb (where, n = charge or valency)

# Volume of the gases evolved at other than NTP

(i) $PV = nRT$

$PV = \frac{m}{M_w} RT \Rightarrow mass = \frac{PV M_w}{RT}$ —(I)

(ii) $mass = ZIt$ —(II)

Hence, $\boxed{ZIt = \frac{PV \times M_w}{RT}}$

# Electrolysis

Reations at cathode & anode.

(i) Oxidation at anode & Reduction at cathode.

(ii) comparing two cations the cation having higher reduction potential gets reduced first.

(iii) comparing two anions the anion having lower reduction potential gets oxidised first.

# ECS: Arranged in order of increasing reduction potential
i.e. $F_2$ → highest R.P & $Li^+$ → lowest R.P.

(I) Li Ke Baba Sardar
Li K Ba Sr

(II) Ca Na Mage Alu Pani me
Ca Na Mg Al $H_2O$

(III) Maine Zinda crow Fry Cardiya
Mn Zn Cr Fe Cd

(IV) Coi Nahi Sung Prabhu Hanuman
Co Ni Sn Pb H

(V) Firse Aunty Me Cl Oxygen Ko
$F_2$ Au $Cl_2$ $O_2$

Peeta Barbar Pen silse Mar Ke
Pt $Br_2$ Pd Ag Hg Cu

# Li K Ba Sr Ca Na Mg Al $H_2O$ Mn Zn Cr Fe Cd

Co Ni Sn Pb (H) Cu Hg Ag Pd $Br_2$ Pt $O_2$ $Cl_2$ Au $F_2$

SRP = -ve ← SRP = 0 → SRP = +ve.

① Reducing Power $\propto \frac{1}{SRP}$ & oxidising power $\propto$ SRP

② Metals higher in series can displace metals at lower position from their salt solution [Active displaces less active]

③ Metals above $H_2$ → release $H_2$ gas on Rxn with dil acid.

④ Elements above → anode & below → cathode.

⑤ $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ { $E^\circ_{cell}$ → +ve → spontaneous; → -ve → non-spontaneous }

→ Out of anions, halide is oxidised first to give halogen. If halides not present then $OH^-$ gets oxidised to give $O_2$.

For a gas at NTP,
At, 11.2 L ⟶ V.D. } V.D = 11.2

# Avogadro's Hypothesis
↳ Equal volume contains equal no. of molecules.

# Gay Lussac's law:-
Whenever gases reacts, they do so in volumes which bear a simple ratio to one another and to the volumes of products. (under similar condition of temp & pressure)

Eg:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

1 vol 3 vol 2 vol.

# Emperical formula (simplest formula)

| Element | % | At. wt. | % / At. wt. (simplest ratio of moles) | |
|---|---|---|---|---|
| X | 50% | x% | 5 | ⟶ whole no. ratio → 2 |
| Y | 50% | (100-x)% | 20 | 2.5 ⟶ whole no. ratio → 1 |

$$\Rightarrow X_2Y$$