Volumetric analysis

- Acidimetry – determination of strength of Alkali with help of Standard solⁿ (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) Hph → 8.2 – 10 ; Litmus (5.5 – 8) }

Permangonometry → $KMnO_4$

Iodometry → starch

- SA & SB → MeOH ; Hph or Litmus (4 – 10)
- SA & WB → MeOH (3 – 8)
- WA & SB → Hph (6 – 11)
- WA & WB → None.

$\boxed{\text{Same Normality of acid is neutralized by alkali having same Vol.}}$

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

20 ml 5N H_2SO_4 =

10 ml 10N H_2SO_4 =

5 ml 20N H_2SO_4 =

5 ml 10M H_2SO_4

Equivalent weight

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

  O ⟶ 8

  Cl ⟶ 35.5

  (ii) $E_{element} = \dfrac{\text{Atomic wt.}}{\text{Valency.}}$

  $\boxed{E = \dfrac{A}{V}}$

- **Acid**:

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

  H attached with O → Basicity

  ↳ Depends on rxn.

  * H_3PO_4 (M) → Eq. wt. = $\dfrac{M}{3}$

  * H_3PO_3 (M) → Eq. wt. = $\dfrac{M}{2}$

  * H_3PO_2 (M) → Eq. wt. = $\dfrac{M}{1}$ = M

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

  ☆ Normality Volume आदि आदि (can exchange numerically)

- **Base**:

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

Trick

Oxide

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

Hydroxide

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

- **Salt**:

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

- $\text{Eq. wt. of radical} = \dfrac{\text{Mass of radical}}{\text{Charge of radical.}}$

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

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 occur in proportion to their gm. eqv.

Concentration terms

① $\%(w/V) = \dfrac{wt.\ of\ solute(in\ g)}{Vol.\ of\ sol^n\ (in\ ml)} \times 100$ { 4% NaOH sol^n by vol ; 4% NaOH sol^n (w/v) ; 4% of NaOH sol^n

② $\%(w/w) = \dfrac{wt.\ of\ solute(in\ g)}{Vol.\ of\ sol^n\ (in\ g)} \times 100$ { 4% NaOH sol^n by wt ; 4% NaOH sol^n (w/w) ; 4% NaOH sol^n (given sp. gravity)

③ $G/L = \dfrac{wt.\ of\ solute\ (in\ g)}{Vol.\ of\ sol^n\ (in\ L)}$

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

$= \dfrac{\dfrac{Amt.\ of\ substance\ dissolved\ (in\ gm)\ \{w\}}{Eqv.\ wt.\ of\ substance\ (E)}}{\dfrac{Vol.\ of\ sol^n\ in\ ml\ (V)}{1000}}$

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

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

$\Rightarrow \boxed{N = \dfrac{w \times 1000}{E \times V}}$ $\boxed{Normality\ factor\ (f) = \dfrac{wt.\ taken}{wt.\ to\ be\ taken}}$

⑤ Molarity (M) $= \dfrac{Amt.\ of\ substance\ dissolved\ in\ mole}{Vol.\ of\ sol^n\ in\ Litre}$ $\boxed{M = \dfrac{(w/v)\% \times 10}{Mol.wt.}}$

$\boxed{No.\ of\ moles = (Vol.\ of\ sol^n\ in\ L) \times M}$ $\boxed{M = \dfrac{w}{M_w} \times \dfrac{1000}{V(in\ ml)}}$ $\boxed{N = \underset{\downarrow\ Acidity,\ Basicity}{X\text{-}factor} \times M}$

⑥ Molality (m) $= \dfrac{Amt.\ of\ substance\ dissolved\ in\ mole}{wt.\ of\ Solvent\ in\ kg.}$ $\boxed{M = \dfrac{(w/w)\% \times sp.gravity \times 10}{mol.wt.}}$

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

⑦ Mole fraction (X)

$\boxed{X_A = \dfrac{n_A}{N_B + n_A}}$ $\boxed{X_B = \dfrac{N_B}{N_B + n_A}}$

{ 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

$\boxed{X_{solution} = X_A + X_B = 1}$ $\boxed{\dfrac{w}{E_w} = \dfrac{V}{E_V}}$ Lt.

Notes

① For complete Rxn b/w ① & ② : $\boxed{N_1 V_1 = N_2 V_2}$

(ii) Strength of mixture :

→ $\boxed{V_m N_m = V_1 N_1 + V_2 N_2 + V_3 N_3}$ { When all sol^n are of same type (ie. acid or alkali)

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

$\boxed{V_m = V_1 + V_2 + V_1' + V_2'}$

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

(iv) Normality × Eq.wt = Molarity × Mol.wt. ⇒ $\boxed{NE = M M_w}$

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

- Temp ↑ ⇒ K_w ↑
- In pure water, $[H^+] = [OH^-]$ & $[H^+] = [OH^-] = 10^{-7}$
- K_w ⇒ constant for given temp.

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

- In acidic solⁿ, $[H^+] > [OH^-]$ ⇒ $[H^+] > 10^{-7}M$
  In Alkaline solⁿ, $[H^+] < [OH^-]$ ⇒ $[H^+] < 10^{-7}M$

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 allcaline solⁿ pH > 7
- For pure water, pH = pOH = 7

~~[H+] = [OH]~~

{$pH = -\log_{10}[H^+]$ ↓ 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

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

HA → concentration C
↳ 1 mole dissolved in V litre

★ $C = \frac{1}{V}$ mole/Litre

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

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

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

- 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). Dissociates slightly in
- Eqᵐ exists b/w undissolved solid & its ions

Eg. $BaSO_{4(s)} \underset{}{\overset{water}{\rightleftharpoons}} BaSO_{4(aq)} \rightleftharpoons Ba^{++}_{(aq)} + SO_4^{--}{(aq)}$

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

K_{sp} for $BaSO_4$ ⇒ solubility product

- Concⁿ 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 $\rightarrow A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}$

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

Solubility $\rightarrow$ 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 $\Rightarrow$ saturated solution.
- $K_{sp} \rightarrow$ constant for given temp.
- In mixture, K_{sp} is constant for solubility changes.
- Solubility $\rightarrow$ expressed in mole per Litre
- (x). $K_{sp} \rightarrow$ constant irrespective of other ions in the solution.
- K_{sp} of salt $\uparrow \Rightarrow$ solubility in water $\uparrow$

Ionic product (Q) $\rightarrow$ product of conc^n of ions in sol^n

- $Q = K_{sp}$, $\Rightarrow$ saturated sol^n & no ppt
- $Q < K_{sp}$ $\Rightarrow$ Unsaturated sol^n & no ppt.
- $Q > K_{sp}$ $\Rightarrow$ Supersaturated sol^n & ppt. occurs
- $Q \rightarrow$ variable & can be measured at any ~~co~~ concentration (sat, unsat. or super sat)

Common-ion effect

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

↳ In ~~prese~~ common-ion effect, solubility differs 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 $\Rightarrow$ No hydrolysis $\Rightarrow$ aq. solution : Neutral

(ii) salt of S.B & W.A $\Rightarrow$ Anions of salt & H^+ of water combines (Anionic hydrolysis) $\Rightarrow$ aq. solution : Basic

Eg: CH_3COONa, $NaCN$, Na_2CO_3

(iii) salt of S.A. & W.B $\Rightarrow$ Cation of salt & OH^- of water combines (Cationic hydrolysis) $\Rightarrow$ aq. solution : Acidic

Eg: NH_4Cl, $CuSO_4$, $FeCl_3$

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

Eg. (iii) $NH_4Cl_{(aq)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$ $\rightarrow HCl$

$\longrightarrow H^+ + OH^- \rightarrow NH_4OH$

NH_4OH (weak electrolyte) $\rightleftharpoons NH_4^+ + OH^-$ } Being weak tries to remain undissociated

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

(S.E) $\rightarrow$ so remains in ionic form $\longrightarrow [H^+] > [OH^-]$

Electrochemistry

$\Delta H = -ve$, $\Delta G = -ve$
$\Delta S = +ve \rightarrow$ spo

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.

i.e.

$W \propto Q$

or, $W = ZQ$

or, $\boxed{W = ZIt}$

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

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),

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

Unit of Z: gram coulomb^{-1}

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

$Z \propto E$

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

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

For 2 substances 1 and 2,

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

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

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 (surface), θ → thickness of plating

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

* Kohlrausch's law,

For infinite dilution,

$$\boxed{\lambda^\circ = \lambda^\circ_+ + \lambda^\circ_-}$$

λ° → eqv. conductance of electrolyte; λ°_+ → eqv. cond. of cation; λ°_- → of anion.

1 mole → molar mass

1 gm equivalent → equivalent mass.

2^{nd} law :- (same current / same charge) $\Rightarrow$ Q same $\Rightarrow$ It same $\Rightarrow$ I (in series) same, 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) $\propto$ chemical equivalent (E)

In terms of Vol. at NTP

$$\frac{V_1}{Eq.Vol._1} = \frac{V_2}{Eq.vol_2}$$

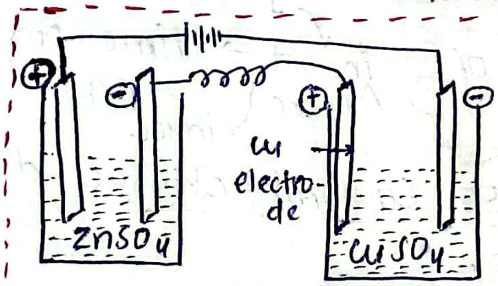
$\boxed{W \propto E}$

or $W = KE$ [$k \rightarrow$ proportionality constant]

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

Accordingly,

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



$m_{zn} = Z_{zn}Q$ — (I) $\quad m_{cu} = Z_{cu}Q$ — (II)

$\hookrightarrow$ mass of Zn deposited

(I) ÷ (II)

$$\frac{m_{zn}}{m_{cu}} = \frac{Z_{zn}}{Z_{cu}}$$

$$\frac{m_{zn}}{m_{cu}} = \frac{E_{zn}/F}{E_{cu}/F}$$

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

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

$\Delta H = \Delta U + \Delta n RT$

$\Delta G = \Delta H - T\Delta S$

* Approx. atomic wt. × sp. heat ≈ 6.4
* specific conductance (K) $= \frac{1}{R} \cdot \frac{l}{A}$
  $\hookrightarrow$ siemens cm^{-1}
* Equivalent conductance (λ) $= \frac{l \times 1000}{R \cdot A \cdot N}$
  $\hookrightarrow$ siemens cm^2 $equiv^{-1}$
* Molar conductance (μ) $= \frac{l \times 1000}{RAM}$
  $\hookrightarrow$ siemens $cm^2 mol^{-1}$

l = length of sep. (cm)
R = Resistance
A = CSA of electrode (cm^2)
N = Normality of soln.
M = Molarity of soln. (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]
  $E \rightarrow$ Emf of cell $\quad F = 96500C$
* $\Delta G = -RT \ln K_{eq}$
* Nerst eq^n, $\rightarrow$ $E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$

$[M] \rightarrow$ Molar conc. of reduced species
$[M^{n+}] \rightarrow$ Molar conc. of oxidised species
[Molar conc. of pure metal is arbitrarily taken as 1]

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

1 mole electron = 1 faraday = 96500C → 1 gm. eqv. (deposit or liberate)

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

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

eg: ① 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 (%) = $\frac{m \times F}{E \times I \times t} \times 100$

No. of charge required to deposit,

1 mole of M^{n+} = nF coulomb (where, n = charge or valency)

Volume of the gas evolved at other than NTP

① $PV = nRT$

$PV = \frac{m}{M_w} RT \Rightarrow mass = \frac{PVM_w}{RT}$ —①

(ii) mass = $\frac{ZIt}{}$ —(ii)

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

Electrolysis

Reactions at cathode & anode.

① Oxidation at anode & Reduction at cathode.

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

① 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 Suna Prabhu Hanuman → Co, Ni, Sn, Pb, H

(V) Firse Aunty Ne 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

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

(iii) Metals above H_2 → release H_2 gas on Rxn with dil acid.

(iv) Elements above → anode & below → cathode.

(v) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ { E°_{cell} → +ve → spontaneous, → -ve → non-spontaneous }

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

For a gas at NTP, $\{ V.D = 11.2$
At, 11.2 L $\longrightarrow$ V.D.

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

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

Eg:

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

N_2 ⇓ 1 vol, $3H_2$ ↓ 3 vol, $2NH_3$ ↓ 2 vol.

Emperical formula (simplest formula)

Element	%	At. wt.	%/At. wt (simplest ratio of moles)		
X	50% x%	10	5	$\longrightarrow$	whole no ratio → 2 (5/2.5)
Y	50% (100−x)%	20	2.5	$\longrightarrow$	whole no ratio → 1 (2.5/2.5)

$\Rightarrow X_2Y$