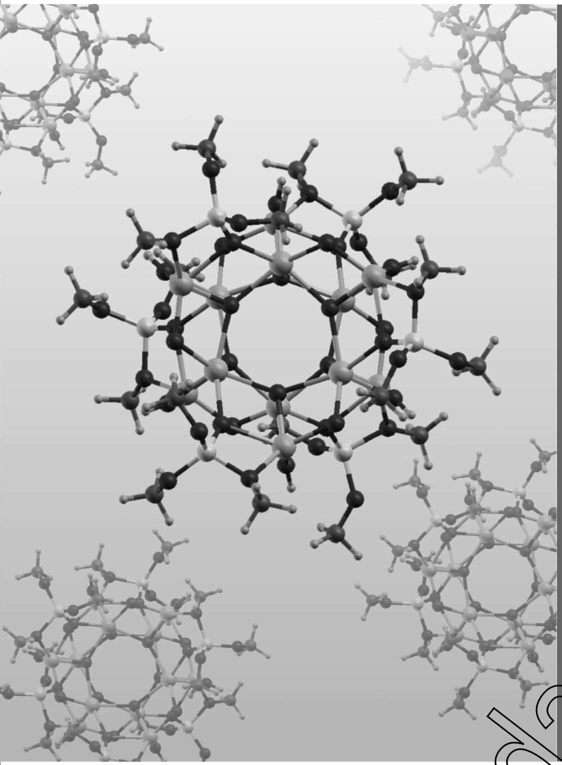
Resonance
Educating for better tomorrow



CHEMISTRY

Formula Book for

Engineering Entrance Examinations

ISEET = IIT JEE + AIEEE + State PETs

(The Gateway to IITs, NITs, IIITs, IISERs & Prominent Engineering/Science Institutions)

www.aimsdaretosuccess.blogspot.com

Best Wishes for

Your Success in Competitive Examinations ahead !!!

This Booklet has been prepared by Resonance for the benefit & academic support to sincere students.
You can send your feedback/suggestion on this booklet at **feedback@resonance.ac.in**

Resonance
Educating for better tomorrow

Admission Announcement

Yearlong Classroom Contact Programme | (Academic Session: 2012-13)

For ISEET (IIT-JEE/AIEEE) | NEET (AIPMT) | SAT | PCCPs

Nurturing Talent... Creating Champions...

From 'Within' You To A 'Winning' You

Grand Success in IIT-JEE 2011

"The **Best Ranks** from **Yearlong Classroom Programmes** in **IIT-JEE 2011** by any Institute in Kota and entire West, East, North & Central India"

SHUBHAM MEHTA
Resonance Roll No.: 912161
Class: XII | Batch: IP
XII Board % (Aggr.): 92.80%
Study Center: Kota
Home Town: Kota

All India Rank
2
General Category

Total Selections in IIT-JEE 2011

1816

(Yearlong Classroom: 1197 | Distance: 619)

17 All India Ranks in TOP-100

(Yearlong Classroom: 13 | Distance: 4)

NISHEETH LAHOTI
Resonance Roll No.: 903807
Class: XII | Batch: IP
XII Board % (Aggr.): 79.60%
Study Center: Kota
Home Town: Kota (Last 5 yrs.)

All India Rank
5
General Category

Shubham & Nisheeth have also won Gold Medal & Silver Medal respectively at 42nd International Physics Olympiad (IPhO) - 2011 held at Bangkok, Thailand

	AIR-14	**AIR-23**	**AIR-26**	**AIR-31**	**AIR-35**	**AIR-36**	**AIR-57**	**AIR-66**	**AIR-87**	**AIR-90**	**AIR-95**
											
NAME	**ARCHIT GUPTA**	**MRIDUL GARG***	**MEHUL GOYAL***	**DIVYAM BANSAL**	**VIVEK AGARWAL**	**GAURAV POONIWALA**	**NEERAJ YADAV**	**ANMOL GARG***	**S. S. KAUSHIK**	**ASTHA AGARWAL***	**GAURAV AHUJA**
RESO ROLL NO.	923350	832206	832414	912162	917367	900978	905427	832229	900425	833069	901110
BATCH IN RESO	IP (Class XII)	PA1 (Class XII)	IP (Class XII)	IP (Class XII)	PB1 (Class XII)	SRP1 (Class XII)	PA1 (Class XII)	PA1 (Class XII)	SRP1 (Class XII)	IJP1 (Class XII)	PA1 (Class XII)
XII BOARD %	90.00%	87.60%	89.40%	93.02%	93.20%	93.33%	72.70%	86.00%	94.83%	93.80%	90.00%
STUDY CENTRE	Kota	Kota	Kota	Kota	Kota	Mumbai	Kota	Kota	Mumbai	Jaipur	Kota
HOME TOWN	Satna	Kota	Kota	Muzaffar Nagar	Agra	Mumbai	Narnaul	Kota	Mumbai	Jaipur	Hisar

***ALSO PCCP STUDENT**

ADMISSION ANNOUNCEMENT

Academic Session 2012-13 | Yearlong Classroom Contact Programmes (YCCPs)

Target: ISEET (IIT-JEE/AIEEE)
Medium: English & Hindi
Admission Through Resonance National Entrance Test (ResoNET) : 2012

Target Year	Class	Date(s) of ResoNET			Test Time
2016	VIII to IX Moving Students	25.03.2012	01.04.2012	15.04.2012	09:00 am to 12:00 noon
2015	IX to X Moving Students	25.03.2012	–	–	
2014	X to XI Moving Students	15.04.2012	20.05.2012	17.06.2012	
2013	XI to XII Moving Students	25.03.2012	15.04.2012	–	
2013	XII Appearing Students	25.03.2012	06.05.2012	10.06.2012	

Target: NEET (AIPMT)
Medium: English & Hindi
DIRECT ADMISSION

Target Year	Class	Date(s) of Course Commencement			
2016	VIII to IX Moving Students	21.05.2012	–	–	–
2015	IX to X Moving Students	02.04.2012	–	–	–
2014	X to XI Moving Students	16.04.2012	01.05.2012	04.06.2012	18.06.2012
2013	XI to XII Moving Students	16.04.2012	14.05.2012	04.06.2012	–
2013	XII Appearing Students	16.04.2012	28.05.2012	18.06.2012	02.07.2012

Target: SAT Reasoning Test
Admission Through Aptitude Test

Target	Class	Date(s) of Aptitude Test		Test Time
SAT 2014	X to XI Moving Students	25.03.2012	06.05.2012	09:00 am to 12:00 noon
SAT 2013	XI to XII Moving Students	25.03.2012	–	

Pre-foundation Career Care Programmes (PCCPs) for **Class VII, VIII, IX & X**
Admission Through Resonance Scholarship cum Admission Test (ResoSAT):2012

ResoSAT Date for Phase-I Admission	ResoSAT Dates for Phase-II Admission		Duration of ResoSAT
25.03.2012	06.05.2012	20.05.2012	90 minutes

How to obtain the Admission Packet

(a) **Online:** Visit www.resonance.ac.in, provide your details and buy ONLINE by paying through Credit/Debit Card & Net Banking.
(b) **In Person:** Through Cash/DD made in favour of 'Resonance', payable at Kota and submit it at Corporate Office, Kota or any of the Resonance Study Centres.
(c) **From AXIS Bank:** Admission Packet is also available at Selected Branches (visit www.resonance.ac.in to see the selected AXIS Bank Branch Locations)
(d) **By Post/ Courier:** Make a DD/Pay Order of required amount in favour of 'Resonance', payable at Kota and send it to Corporate Office at Kota only.
(e) **By VPP:** Call on our Toll Free No. & provide your details. The Admission Packet will be sent to your home through VPP & payment can be made when you receive it.

COST OF ADMISSION PACKET: For ISEET (IIT-JEE/AIEEE) Courses: ₹ 1000/- | For NEET (AIPMT)/SAT Courses: ₹ 500/- | For PCCP Courses: ₹ 200/-

Note: If you make DD for Admission Packet then please mention your name, father's name, class in which studying presently, postal address and contact/mobile numbers on the backside of the bank DD. Also keep the photocopy of DD with you for future reference.

Resonance Eduventures Pvt. Ltd.

CORPORATE OFFICE: CG Tower, A-46 & 52, Near City Mall, Jhalawar Road, Kota (Raj.) - 324005 | **Tel.:** 0744-3192222, 3012222, 3022222, 2437144

To Know more: sms RESO at 56677 | Toll Free : 1800 200 2244 | contact@resonance.ac.in | www.resonance.ac.in | WAPsite: m.resonance.ac.in

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SHORT FORMULA (GYAN SUTRA)

CHEMISTRY

PHYSICAL CHEMISTRY

ATOMIC STRUCTURE

Estimation of closest distance of approach (derivation) of α-particle : $R = \dfrac{4KZe^2}{m_\alpha V_\alpha{}^2}$

The radius of a nucleus : $R = R_0 (A)^{1/3}$ cm

Planck's Quantum Theory : Energy of one photon = $h\nu = \dfrac{hc}{\lambda}$

Photoelectric Effect : $h\nu = h\nu_0 + \dfrac{1}{2} m_e v^2$

Bohr's Model for Hydrogen like atoms :

1. $mvr = n \dfrac{h}{2\pi}$ (Quantization of angular momentum)

2. $E_n = -\dfrac{E_1}{n^2} z^2 = 2.178 \times 10^{-18} \dfrac{z^2}{n^2}$ J/atom $= 13.6 \dfrac{z^2}{n^2}$ eV ; $E_1 = \dfrac{-2\pi^2 me^4}{n^2}$

3. $r_n = \dfrac{n^2}{Z} \times \dfrac{h^2}{4\pi^2 e^2 m} = \dfrac{0.529 \times n^2}{Z}$ Å

4. $v = \dfrac{2\pi ze^2}{nh} = \dfrac{2.18 \times 10^6 \times z}{n}$ m/s

De–Broglie wavelength :

$\lambda = \dfrac{h}{mc} = \dfrac{h}{p}$ (for photon)

Wavelength of emitted photon :

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

No. of photons emitted by a sample of H atom :

$$\frac{\Delta n(\Delta n + 1)}{2}$$

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Heisenberg's uncertainty principle :

$\Delta x.\Delta p > \frac{h}{4\pi}$ or $m\,\Delta x.\Delta v \geq \frac{h}{4\pi}$ or $\Delta x.\Delta v \geq \frac{h}{4\pi m}$

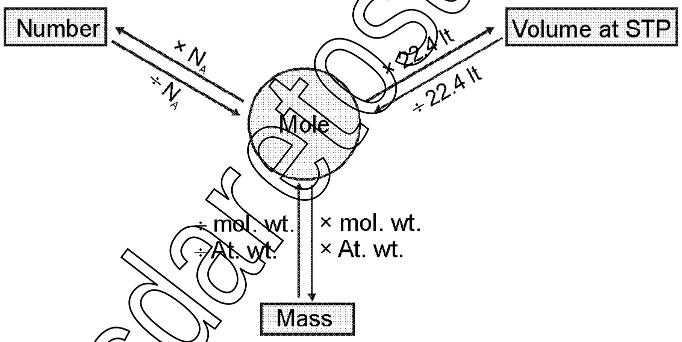
Quantum Numbers :

- * Principal quantum number (n) = 1, 2, 3, 4 .... to ∞.
- * Orbital angular momentum of electron in any orbit = $\frac{nh}{2\pi}$.
- * Azimuthal quantum number (ℓ) = 0, 1, ... to (n – 1).
- * Number of orbitals in a subshell = $2\ell + 1$
- * Maximum number of electrons in particular subshell = $2 \times (2\ell + 1)$
- * Orbital angular momentum $L = \frac{h}{2\pi}\sqrt{\ell(\ell+1)} = \hbar\sqrt{\ell(\ell+1)}$ $\left[\hbar = \frac{h}{2\pi}\right]$

STOICHIOMETRY

☞ Relative atomic mass (R.A.M) = $\frac{\text{Mass of one atom of an element}}{\frac{1}{12}\times\text{mass of one carbon atom}}$ = Total Number of nucleons

☞ <u>**Y-map**</u>



Density :

Specific gravity = $\frac{\text{density of the substance}}{\text{density of water at } 4^\circ\text{C}}$

For gases :

Absolute density (mass/volume) = $\frac{\text{Molar mass of the gas}}{\text{Molar volume of the gas}}$ ⇒ $\rho = \frac{PM}{RT}$

Vapour density $\text{V.D.} = \frac{d_{gas}}{d_{H_2}} = \frac{PM_{gas/RT}}{PM_{H_2/RT}} = \frac{M_{gas}}{M_{H_2}} = \frac{M_{gas}}{2}$

$M_{gas} = 2\ \text{V.D.}$

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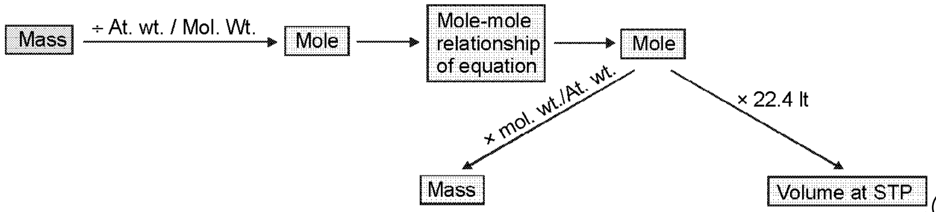
Mole-mole analysis :



Concentration terms :

Molarity (M) :

$\therefore$ Molarity (M) = $\dfrac{w \times 1000}{(\text{Mol. wt of solute}) \times V_{\text{inml}}}$

Molality (m) :

Molality = $\dfrac{\text{number of moles of solute}}{\text{mass of solvent in gram}} \times 1000$ = $1000\ w_1 / M_1 w_2$

Mole fraction (x) :

$\therefore$ Mole fraction of solution (x_1) = $\dfrac{n}{n+N}$ $\therefore$ Mole fraction of solvent (x_2) = $\dfrac{N}{n+N}$

$x_1 + x_2 = 1$

% Calculation :

(i) % w/w = $\dfrac{\text{mass of solute in gm}}{\text{mass of solution in gm}} \times 100$

(ii) % w/v = $\dfrac{\text{mass of solute in gm}}{\text{mass of solution in ml}} \times 100$

(iii) % v/v = $\dfrac{\text{Volume of solution in ml}}{\text{Volume of solution}} \times 100$

Derive the following conversion :

1. Mole fraction of solute into molarity of solution M = $\dfrac{x_2 \rho \times 1000}{x_1 M_1 + M_2 x_2}$

2. Molarity into mole fraction x_2 = $\dfrac{MM_1 \times 1000}{\rho \times 1000 - MM_2}$

3. Mole fraction into molality m = $\dfrac{x_2 \times 1000}{x_1 M_1}$

4. Molality into mole fraction x_2 = $\dfrac{mM_1}{1000 + mM_1}$

5. Molality into molarity M = $\dfrac{m\rho \times 1000}{1000 + mM_2}$

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6. Molarity into Molality m = $\frac{M \times 1000}{1000\rho - MM_2}$

M_1 and M_2 are molar masses of solvent and solute. ρ is density of solution (gm/mL)
M = Molarity (mole/lit.), m = Molality (mole/kg), x_1 = Mole fraction of solvent, x_2 = Mole fraction of solute

Average/Mean atomic mass :

$$A_x = \frac{a_1x_1 + a_2x_2 + ... + a_nx_n}{100}$$

Mean molar mass or molecular mass :

$$M_{avg.} = \frac{n_1M_1 + n_2M_2 + ...n_nM_n}{n_1 + n_2 + ...n_n} \quad \text{or} \quad M_{avg.} = \frac{\sum_{j=1}^{j=n} n_jM_j}{\sum_{j=1}^{j=n} n_j}$$

Calculation of individual oxidation number :

Formula : Oxidation Number = number of electrons in the valence shell – number of electrons left after bonding

Concept of Equivalent weight/Mass :

For elements, equivalent weight (E) = $\frac{\text{Atomic weight}}{\text{Valency - factor}}$

For acid/base, $E = \frac{M}{\text{Basicity / Acidity}}$ Where M = Molar mass

For O.A/R.A, $E = \frac{M}{\text{no. of moles of } e^- \text{ gained / lost}}$

Equivalent weight (E) = $\frac{\text{Atomic or moleculear weight}}{\text{v.f.}}$ **(v.f. = valency factor)**

Concept of number of equivalents :

No. of equivalents of solute = $\frac{Wt}{Eq.\ wt.} = \frac{W}{E} = \frac{W}{M/n}$

No. of equivalents of solute = No. of moles of solute × v.f.

Normality (N) :

Normality (N) = $\frac{\text{Number of equivalents of solute}}{\text{Volume of solution (in litres)}}$

Normality = Molarity × v.f.

Calculation of valency Factor :

n-factor of acid = basicity = no. of H^+ ion(s) furnished per molecule of the acid.

n-factor of base = acidity = no. of OH^- ion(s) furnised by the base per molecule.

At equivalence point :

$N_1V_1 = N_2V_2$

$n_1M_1V_1 = n_2M_2V_2$

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Volume strength of H_2O_2:

20V H_2O_2 means **one litre** of this sample of H_2O_2 on decomposition gives **20 lt. of O_2** gas at **S.T.P.**

$$\text{Normality of } H_2O_2 \text{ (N)} = \frac{\text{Valume, strength of } H_2O_2}{5.6}$$

$$\textbf{Molarity of } \mathbf{H_2O_2 (M)} = \frac{\textbf{Volume strength of } \mathbf{H_2O_2}}{\mathbf{11.2}}$$

Measurement of Hardness :

$$\textit{Hardness in ppm} = \frac{\text{mass of } CaCO_3}{\text{Total mass of water}} \times 10^6$$

Calculation of available chlorine from a sample of bleaching powder :

$\% \text{ of } Cl_2 = \dfrac{3.55 \times x \times V\,(mL)}{W(g)}$ where x = molarity of hypo solution and v = mL. of hypo solution used in titration.

GASEOUS STATE

Temperature Scale :

$\dfrac{C-O}{100-0} = \dfrac{K-273}{373-273} = \dfrac{F-32}{212-32} = \dfrac{R-R(O)}{R(100)-R(O)}$ where R = Temp. on unknown scale.

Boyle's law and measurement of pressure :

At constant temperature, $V \alpha \dfrac{1}{P}$

$$P_1V_1 = P_2V_2$$

Charles law :

At constant pressure, $V \alpha T$ or $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

Gay-lussac's law :

At constant volume, $P \alpha T$

$\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$ → temp on absolute scale

Ideal gas Equation :

$$PV = nRT$$

$PV = \dfrac{w}{m} RT$ or $P = \dfrac{d}{m} RT$ or $Pm = dRT$

Daltons law of partial pressure :

$P_1 = \dfrac{n_1 RT}{v}$, $P_2 = \dfrac{n_2 RT}{v}$, $P_3 = \dfrac{n_3 RT}{v}$ and so on.

Total pressure = $P_1 + P_2 + P_3 + \ldots\ldots\ldots$

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Partial pressure = mole fraction X Total pressure.

Amagat's law of partial volume :

$$V = V_1 + V_2 + V_3 + ...$$

Average molecular mass of gaseous mixture :

$$M_{mix} = \frac{\text{Total mass of mixture}}{\text{Total no. of moles in mixture}} = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

Graham's Law :

Rate of diffusion $r \propto \frac{1}{\sqrt{d}}$; d = density of gas

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} = \sqrt{\frac{V.D_2}{V.D_1}}$$

Kinetic Theory of Gases :

$PV = \frac{1}{3}\, mN\, \overline{U^2}$ Kinetic equation of gases

Average K.E. for one mole = $N_A \left(\frac{1}{2} m\, \overline{U^2}\right) = \frac{3}{2}\, K N_A T = \frac{3}{2} RT$

☞ Root mean suqare speed

$U_{rms} = \sqrt{\frac{3RT}{M}}$ molar mass must be in kg/mole.

☞ Average speed

$$U_{av} = U_1 + U_2 + U_3 + ... U_N$$

$U_{avg.} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}}$ K is Boltzmman constant

☞ Most probable speed

$$U_{MPS} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2KT}{m}}$$

Vander wall's equation :

$$\left(P + \frac{an^2}{v^2}\right)(v - nb) = nRT$$

☞ **Critical constants :**

$V_c = 3b$, $P_C = \frac{a}{27b^2}$, $T_C = \frac{8a}{27Rb}$

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Vander wall equation in virial form :

$$Z = \left(1+\frac{b}{V_m}+\frac{b^2}{V_m^2}+\frac{b^3}{V_m^3}+\ldots\ldots\ldots\right) - \frac{a}{V_m RT} = 1 + \frac{1}{V_m}\left(b-\frac{a}{RT}\right) + \frac{b^2}{V_m^2} + \frac{b^3}{V_m^3} + \ldots\ldots\ldots\ldots\ldots\ldots$$

Reduced Equation of state :

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8\,T_r$$

THERMODYNAMICS

Thermodynamic processes :

1. **Isothermal process :** T = constant
   dT = 0
   $\Delta T = 0$
2. **Isochoric process :** V = constant
   dV = 0
   $\Delta V = 0$
3. **Isobaric process :** P = constant
   dP = 0
   $\Delta P = 0$
4. **Adiabatic process :** q = 0
   or heat exchange with the surrounding = 0(zero)

IUPAC Sign convention about Heat and Work :

Work done on the system = Positive
Work done by the system = Negative
1st Law of Thermodynamics

$$\Delta U = (U_2 - U_1) = q + w$$

Law of equipartion of energy :

$$U = \frac{f}{2} nRT \quad \textbf{(only for ideal gas)}$$

$$\Delta E = \frac{f}{2} nR\,(\Delta T)$$

where f = degrees of freedom for that gas. (Translational + Rotational)
f = 3 for monoatomic
= 5 for diatomic or linear polyatmic
= 6 for non - linear polyatmic

Calculation of heat (q) :
Total heat capacity :

$$C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = \text{J/}^{\circ}\text{C}$$

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Molar heat capacity :

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} = J\ mole^{-1} K^{-1}$$

$$C_P = \frac{\gamma R}{\gamma - 1} \qquad C_V = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} = Jgm^{-1} K^{-1}$$

WORK DONE (w) :

Isothermal Reversible expansion/compression of an ideal gas :

$$W = -\,nRT \ln (V_f/V_i)$$

Reversible and irreversible isochoric processes.

Since $dV = 0$

So $dW = -\,P_{ext} . dV = 0.$

Reversible isobaric process :

$$W = P\,(V_f - V_i)$$

Adiabatic reversible expansion :

$$\Rightarrow \qquad T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$$

Reversible Work :

$$\mathbf{W} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR\,(T_2 - T_1)}{\gamma - 1}$$

Irreversible Work :

$$\mathbf{W} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR\,(T_2 - T_1)}{\gamma - 1} \quad nC_v\,(T_2 - T_1) = -\,P_{ext}\,(V_2 - V_1) \text{ and use } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Free expansion – Always going to be irrerversible and since $P_{ext} = 0$

so $dW = -\,P_{ext} . dV = 0$

If no. heat is supplied $q = 0$

then $\Delta E = 0$ so $\Delta T = 0.$

Application of Ist Law :

$$\Delta U = \Delta Q + \Delta W \qquad \Rightarrow \qquad \Delta W = -P\,\Delta V$$

$$\therefore \qquad \Delta U = \Delta Q - P\Delta V$$

Constant volume process

Heat given at constant volume = change in internal energy

$\therefore\ du = (dq)_v$

$du = nC_v dT$

$$C_v = \frac{1}{n}.\frac{du}{dT} = \frac{f}{2}R$$

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Constant pressure process :

H ≡ Enthalpy (state function and extensive property)

$$H = U + PV$$

$\Rightarrow$ **$C_p - C_v = R$ (only for ideal gas)**

Second Law Of Thermodynamics :

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ for a spontaneous process.

Entropy (S) :

$$\Delta S_{\text{system}} = \int_A^B \frac{dq_{\text{rev}}}{T}$$

Entropy calculation <u>for an ideal gas</u> undergoin a process :

State A $\xrightarrow[\Delta S_{\text{irr}}]{\text{irr}}$ State B

P_1, V_1, T_1 P_2, V_2, T_2

$\Delta S_{\text{system}} = nc_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ (only for an ideal gas)

Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Gibb's free energy (G) : (State function and an extensive property)

$$G_{\text{system}} = H_{\text{system}} - TS_{\text{system}}$$

Criteria of spontaneity :

(i) If ΔG_{system} is (–ve) < 0 $\Rightarrow$ process is spontaneous

(ii) If ΔG_{system} is > 0 $\Rightarrow$ process is non spontaneous

(iii) If $\Delta G_{\text{system}} = 0$ $\Rightarrow$ system is at equilibrium.

Physical interpretation of ΔG :

→ The maximum amount of non-expansional (compression) work which can be performed.

$$\Delta G = dw_{\text{non-exp}} = dH - TdS.$$

Standard Free Energy Change (ΔG^o) :

1. $\Delta G^o = -2.303\ RT \log_{10} K$

2. At equilibrium $\Delta G = 0$.

3. The decrease in free energy ($-\Delta G$) is given as :

$$-\Delta G = W_{\text{net}} = 2.303\ nRT \log_{10} \frac{V_2}{V_1}$$

4. ΔG_f° for elemental state = 0

5. $\Delta G_f^{\circ} = G^{\circ}_{\text{products}} - G^{\circ}_{\text{Reactants}}$

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Thermochemistry :

Change in standard enthalpy $\Delta H^\circ = H^0_{m,2} - H^0_{m,1}$

$= \text{heat added at constant pressure.} = C_P\Delta T.$

If $H_{products} > H_{reactants}$

→ Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

and if $H_{products} < H_{reactants}$

→ Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction : $\Delta H_{reaction} = H_{products} - H_{reactants}$

$\Delta H^\circ_{reactions} = H^\circ_{products} - H^\circ_{reactants}$

= positive – endothermic

= negative – exothermic

Temperature Dependence Of ΔH : (Kirchoff's equation) :

For a constant volume reaction

$\Delta H_2^\circ = \Delta H_1^\circ + \Delta C_P\,(T_2 - T_1)$

where $\Delta C_P = C_P\,(\text{products}) - C_P\,(\text{reactants})$.

For a constant volume reaction

$$\Delta E_2^0 = \Delta E_1^0 + \int \Delta C_V\,.dT$$

Enthalpy of Reaction from Enthalpies of Formation :

The enthalpy of reaction can be calculated by

$\Delta H_r^\circ = \Sigma\,\nu_B\,\Delta H_f^\circ,_{products} - \Sigma\,\nu_B\,\Delta H_f^\circ,_{reactants}$ ν_B is the stoichiometric coefficient.

Estimation of Enthalpy of a reaction from bond Enthalpies :

$$\Delta H = \begin{pmatrix}\text{Enthalpy required to}\\ \text{break reactants into}\\ \text{gasesous atoms}\end{pmatrix} - \begin{pmatrix}\text{Enthalpy released to}\\ \text{form products from the}\\ \text{gasesous atoms}\end{pmatrix}$$

Resonance Energy :

$\Delta H^\circ_{resonance} = \Delta H^\circ_{f,\,experimental} - \Delta H^\circ_{f,\,calclulated}$

$= \Delta H^\circ_{c,\,calculated} - \Delta H^\circ_{c,\,experimental}$

CHEMICAL EQUILIBRIUM

At equilibrium :

(i) Rate of forward reaction = rate of backward reaction

(ii) Concentration (mole/litre) of reactant and product becomes constant.

(iii) $\Delta G = 0$.

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(iv) $Q = K_{eq.}$

Equilibrium constant (K) :

$$K = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}} = \frac{K_f}{K_b}.$$

Equilibrium constant in terrms of concentration (K_C) :

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

Equilibrium constant in terms of partial pressure (K_P) :

$$K_P = \frac{[P_C]^c\ [P_D]^d}{[P_A]^a\ [P_B]^b}$$

Equilibrium constant in terms of mole fraction (K_x) :

$$K_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$$

Relation between K_p & K_c :

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

Relation between K_p & K_x :

$K_P = K_x\ (P)^{\Delta n}$

* $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$; ΔH = Enthalpy of reaction

Relation between equilibrium constant & standard free energy change :

$\Delta G^o = -\ 2.303\ RT \log K$

Reaction Quotient (Q) :

The values of expression $Q = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$

Degree of Dissociation (α) :

α *= no. of moles dissociated / initial no. of moles taken*

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = α x 100

Observed molecular weight and Observed Vapour Density of the mixture :

Observed molecular weight of A_n(g) = $\frac{\text{molecular weight of equilibrium mixture}}{\text{total no. of moles}}$

$$\alpha = \frac{D - d}{(n-1) \times d} = \frac{M_T - M_o}{(n-1)M_0}$$

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External factor affecting equilibrium :

Le Chatelier's Principle:

If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors that determine the state of equilibrium, the system will react in such a way as to minimize the effect of the disturbance.

Effect of concentration :

* If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .

* If the concentration of product is increased then equilibrium shifts in the backward direction

Effect of volume :

* If volume is increased pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.

* If volume is increased then, for

$\Delta n > 0$ reaction will shift in the forward direction

$\Delta n < 0$ reaction will shift in the backward direction

$\Delta n = 0$ reaction will not shift.

Effect of pressure :

* If pressure is increased at equilibrium then reaction will try to decrease the pressure, hence it will shift in the direction in which less no. of moles of gases are formed.

Effect of inert gas addition :

(i) Constant pressure :

If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed

$\Delta n > 0$ reaction will shift in the forward direction

$\Delta n < 0$ reaction will shift in the backward direction

$\Delta n = 0$ reaction will not shift.

(ii) Constant volume :

Inert gas addition has no effect at constant volume.

Effect of Temperature :

Equilibrium constant is only dependent upon the temperature.

If plot of ℓnk vs $\frac{1}{T}$ is plotted then it is a straight line with slope = $-\frac{\Delta H^\circ}{R}$, and intercept = $\frac{\Delta S^\circ}{R}$

* For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature

* For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

* For $\Delta H > 0$, reaction shiffts in the forward direction with increase in temperatutre

* For $\Delta H < 0$, reaction shifts in the backward direction with increases in temperature.

* If the concentration of reactant is increased at equilibrium then reaction shift in the forward direction .

* If the concentration of product is increased then equilibrium shifts in the backward direction

Vapour Pressure of Liquid :

Relative Humidity = $\frac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temp.}}$

Thermodynamics of Equilibrium :

$$\Delta G = \Delta G^0 + 2.303\ RT\ \log_{10} Q$$

Vant Hoff equation- $\log\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^0}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

IONIC EQUILIBRIUM

1. **OSTWALD DILUTION LAW :**

- Dissociation constant of weak acid (K_a) , $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[C\alpha][C\alpha]}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$

  If $\alpha << 1$, then $1 - \alpha \cong 1$ or $K_a = c\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times V}$

- Similarly for a weak base , $\alpha = \sqrt{\frac{K_b}{C}}$. Higher the value of K_a / K_b , strong is the acid / base.

Acidity and pH scale :

∴ $pH = -\log a_{H^+}$ (where a_{H^+} is the activity of H^+ ions = molar concentration for dilute solution).

[Note : pH can also be negative or > 14]

$pH = -\log [H^+]$;	$[H^+] = 10^{-pH}$
$pOH = -\log [OH^-]$;	$[OH^-] = 10^{-pOH}$
$pKa = -\log Ka$;	$Ka = 10^{-pKa}$
$pKb = -\log Kb$;	$Kb = 10^{-pKb}$

PROPERTIES OF WATER :

1. **In pure water $[H^+] = [OH^-]$ so it is Neutral.**
2. **Moler concentration / Molarity of water = 55.56 M.**
3. **Ionic product of water (K_w) :**
   $K_w = [H^+][OH^-] = 10^{-14}$ at 25° (experimentally)
   pH = 7 = pOH ⇒ neutral
   pH < 7 or pOH > 7 ⇒ acidic
   pH > 7 or pOH < 7 ⇒ Basic
4. **Degree of dissociation of water :**

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18x10^{-10} \text{ or } 1.8x10^{-7}\%$$

5. **Absolute dissociation constant of water :**

$$K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

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$pK_a = pK_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$

$\mathbf{K_a \times K_b = [H^+][OH^-] = K_w}$

$\Rightarrow$ **Note: for a conjugate acid- base pairs**

$pK_a + pK_b = pK_w = 14$ at 25ºC.

pK_a of H_3O^+ ions = –1.74

pK_b of OH^- ions = –1.74.

❍ pH Calculations of Different Types of Solutions :

(a) Strong acid solution :

(i) If concentration is greater than 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

(b) Strong base solution :

Using similar method as in part (a) calculate first $[OH^-]$ and then use $[H^+] \times [OH^-] = 10^{-14}$

(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

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

(d) pH of mixture of two strong bases :

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

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

If $N_1V_1 > N_2V_2$, then solution will be acidic in nature and $[H^+] = N = \dfrac{N_1V_1 - N_2V_2}{V_1 + V_2}$

If $N_2V_2 > N_1V_1$, then solution will be basic in nature and $[OH^-] = N = \dfrac{N_2V_2 - N_1V_1}{V_1 + V_2}$

(f) pH of a weak acid(monoprotic) solution :

$$K_a = \frac{[H^+][OH^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

if $\alpha << 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\dfrac{K_a}{C}}$ (is valid if α < 0.1 or 10%)

On increasing the dilution $\Rightarrow$ $C\downarrow \Rightarrow \alpha\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

(g) pH of a solution of a polyprotic weak acid :

$$\mathbf{pH} = \frac{1}{2}\left(pK_{a_1} - \log C\right).$$

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RELATIVE STRENGTH OF TWO ACIDS :

$$\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{c_1\alpha_1}{c_2\alpha_2} = \sqrt{\frac{k_{a_1}c_1}{k_{a_2}c_2}}$$

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

$$(\alpha_1 << 1) \text{ and } (\alpha_2 << 1) \Rightarrow \frac{K_{a1}}{K_{a2}} = \frac{\alpha_1}{\alpha_2}$$

$$[H^+] = C_1\alpha_1 + C_2\alpha_2 = \sqrt{C_1K_{a1} + C_2K_{a2}}$$

**** If water is again considered third weak acid in solution of two weak acid then**

$$[H^+] = \sqrt{K_{a1}C_1 + K_{a2}C_2 + K_w}$$

$$C_wK_{aw} = 10^{-14} = K_w$$

$$[H^+] = \sqrt{C_1K_{a1} + C_2K_{a2} + 10^{-14}}$$

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

If $[SA] = C_1$ and $[WA] = C_2$, then $[H^+]$ from SA = C_1 and $[H^+]$ from WA = C_2

Let HA is a weak acid.

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_a.C_2}}{2}$$

**** If a strong acid of low conc is added in water then $[H^+]$ of solution can be calculated as**

$$[H^+] = \frac{C_1 + \sqrt{C_1^2 + 4K_w}}{2}.$$

❍ SALT HYDROLYSIS :

	Salt of	Type of hydrolysis	k_h	h	pH
(a)	weak acid & strong base	anionic	$\frac{k_w}{k_a}$	$\sqrt{\frac{k_w}{k_a c}}$	$7 + \frac{1}{2} pk_a + \frac{1}{2} \log c$
(b)	strong acid & weak base	cationic	$\frac{k_w}{k_b}$	$\sqrt{\frac{k_w}{k_b c}}$	$7 - \frac{1}{2} pk_b - \frac{1}{2} \log c$
(c)	weak acid & weak base	both	$\frac{k_w}{k_a k_b}$	$\sqrt{\frac{k_w}{k_a k_b}}$	$7 + \frac{1}{2} pk_a - \frac{1}{2} pk_b$
(d)	Strong acid & strong base	--------do not hydrolysed-------			pH = 7

Hydrolysis of ployvalent anions or cations

For $[Na_3PO_4] = C$.

$$K_{a1} \times K_{h3} = K_w$$

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$$\mathbf{K_{a1} \times K_{h2} = K_w}$$

$$\mathbf{K_{a3} \times K_{h1} = K_w}$$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h1} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h1}}{c}} \quad \Rightarrow [OH^-] = ch = \sqrt{K_{h1} \times c} \quad \Rightarrow [H^+] = \sqrt{\frac{\mathbf{K_W \times K_{a3}}}{\mathbf{C}}}$$

So $$\mathbf{pH = \frac{1}{2}[pK_w + pK_{a3} + \log C]}$$

Hydrolysis of Amphiprotic Anion. (Cation is not Hydrolysed e.g. $NaHCO_3$, NaHS, etc.)

$$pH\ (HCO_3^-) = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right)$$

(b) Similarly for $H_2PO_4^-$ and HPO_4^{2-} amphiprotic anions.

$$pH_{(H_2PO_4^-)} = \left(\frac{pK_{a_1} + pK_{a_2}}{2}\right) \quad \text{and} \quad pH_{(HPO_4^{2-})} = \left(\frac{pK_{a_2} + pK_{a_3}}{2}\right)$$

○ $$H_3PO_4 \xrightarrow{K_{a1}} H_2PO_4^- \xrightarrow{K_{a2}} HPO_4^{2-} \xrightarrow{K_{a3}} PO_4^{3-} \text{ ionisation.}$$

$$\xleftarrow[K_{h_1}=\frac{K_w}{K_{a_1}}]{} \quad \xleftarrow[K_{h2}=\frac{K_w}{k_{a2}}]{} \quad \xleftarrow[K_{h1}=\frac{K_w}{K_{a3}}]{}$$

The pH of $H_3PO_4 = \frac{1}{2}(pK_{a1} - \log C)$ $\quad \because K_{a1} >> K_{a2} >> K_{a3}$

pH of $NaH_2PO_4 = \frac{1}{2}(pK_{a1} + pK_{a2})$

pH of $Na_2HPO_4 = \frac{1}{2}(pK_{a2} + pK_{a3})$

pH of $Na_3PO_4 = \frac{1}{2}(pKw + pKa_3 + \log C)$ $\therefore$ Sec hydrolysis can neglect.

BUFFER SOLUTION :

(a) Acidic Buffer : e.g. CH_3COOH and CH_3COONa. (weak acid and salt of its conjugate base).

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \qquad \text{[Henderson's equation]}$$

(b) Basic Buffer : e.g. $NH_4OH + NH_4Cl$. (weak base and salt of its conjugate acid).

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

Buffer capacity (index) :

$$\text{Buffer capacity} = \frac{\text{Total no. of moles of acid / alkali added per litre}}{\text{Change in pH}}$$

$$\text{Buffer capacity} = \frac{dx}{d\Delta pH} = 2.303\frac{(a+x)(b-x)}{a+b}$$

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INDICATOR :

$$HIn \rightleftharpoons H^+ + In^-$$

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

$$\therefore \quad pH = pK_{HIn} + \log\frac{[In^-]}{[HIn]} \quad \Rightarrow \quad pH = pK_{HIn} + \log\frac{[\text{Ionised form}]}{[\text{Unionised form}]}$$

SIGNIFICANCE OF INDICATORS :

☞ Extent of reaction of different bases with acid (HCl) using two indicators :

	Phenolphthalein	**Methyl Orange**
NaOH	100% reaction is indicated $NaOH + HCl \rightarrow NaCl + H_2O$	100% reaction is indicated $NaOH + HCl \rightarrow NaCl + H_2O$
Na_2CO_3	50% reaction upto $NaHCO_3$ stage is indicated $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	100% reaction is indicated $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3$	No reaction is indicated	100% reaction is indicated $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$.

❍ **ISOELECTRIC POINT :**

$$[H^+] = \sqrt{K_{a1}K_{a2}}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}.$$

SOLUBILITY PRODUCT :

$$K_{SP} = (xs)^x\,(ys)^y = x^x.y^y.(s)^{x+y}$$

CONDITION FOR PRECIPITATION :

If ionic product $K_{I.P} > K_{SP}$ precipitation occurs,

if $K_{I.P} = K_{SP}$ saturated solution (precipitation just begins or is just prevented).

ELECTROCHEMISTRY

ELECTRODE POTENTIAL

For any electrode → oxidiation potential = – Reduction potential

E_{cell} = R.P of cathode – R.P of anode

E_{cell} = R.P. of cathode + O.P of anode

E_{cell} is always a +ve quantity & Anode will be electrode of low R.P

E°_{Cell} = SRP of cathode – SRP of anode.

❍ **Greater the SRP value greater will be oxidising power.**

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GIBBS FREE ENERGY CHANGE :

$$\Delta G = -\,nFE_{cell}$$
$$\Delta G^{o} = -\,nFE^{o}_{cell}$$

NERNST EQUATION : (Effect of concentration and temp of an emf of cell)

⇒ $\Delta G = \Delta G^{o} + RT\,\ell nQ$ (where Q is raection quotient)

$\Delta G^{o} = -\,RT\,\ell n\,K_{eq}$

$$E_{cell} = E^{o}_{cell} - \frac{RT}{nF}\,\ell n\,Q$$

$$E_{cell} = E^{o}_{cell} - \frac{2.303\,RT}{nF}\log Q$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log Q \qquad \text{[At 298 K]}$$

At chemical equilibrium

$\Delta G = 0$; $E_{cell} = 0$.

❍ $$\log K_{eq} = \frac{nE^{o}_{cell}}{0.0591}.$$

$$E^{o}_{cell} = \frac{0.0591}{n}\log K_{eq}$$

For an electrode M(s)/M^{n+}.

$$E_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}]}.$$

CONCENTRATION CELL : A cell in which both the electrods are made up of same material.

For all concentration cell $E^{o}_{cell} = 0$.

(a) Electrolyte Concentration Cell :

eg. $Zn(s) / Zn^{2+}(c_1) \,||\, Zn^{2+}(c_2) / Zn(s)$ $\quad E = \frac{0.0591}{2}\log\frac{C_2}{C_1}$

(b) Electrode Concentration Cell :

eg. $Pt, H_2(P_1\ atm) / H^+(1M) / H_2(P_2\ atm) / Pt$ $\quad E = \frac{0.0591}{2}\log\left(\frac{P_1}{P_2}\right)$

DIFFERENT TYPES OF ELECTRODES :

1. Metal-Metal ion Electrode M(s)/M^{n+}. $\quad M^{n+} + ne^- \longrightarrow M(s) \quad E = E^{o} + \frac{0.0591}{n}\log[M^{n+}]$
2. Gas-ion Electrode $\quad Pt / H_2(Patm) / H^+(XM)$

as a reduction electrode $\quad H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2\,(Patm) \quad E = E^{o} - 0.0591\log\frac{P_{H_2}^{\frac{1}{2}}}{[H^+]}$

3. Oxidation-reduction Electrode Pt / Fe^{2+}, Fe^{3+}

as a reduction electrode $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $E = E^o - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$

4. Metal-Metal insoluble salt Electrode eg. Ag/AgCl, Cl^-

as a reduction electrode $AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$

- $E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag}$ **– 0.0591 log [Cl⁻].**

CALCULATION OF DIFFERENT THERMODYNAMICS FUNCTION OF CELL REACTION

- $\Delta G = -n F E_{cell}$
- $S = -\left[\frac{dG}{dT}\right]_p$ (At costant pressure).
- $\Delta S = -\left[\frac{d(\Delta G)}{dT}\right]_P = nF\left(\frac{d}{dt}(E_{cell})\right)_p$
- $\left[\frac{\partial E}{\partial T}\right]_p$ = Temperature cofficient of e.m.f of the cell.

$E = a + bT + CT^2 + ...$

- $\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_p - E\right]$
- **ΔCp of cell reaction**

$Cp = \frac{dH}{dT}$

$\Delta Cp = \frac{d}{dT}(\Delta H)$

$\Delta C_p = n F T \frac{d^2E_{cell}}{dT^2}$

- **ELECTROLYSIS :**

(a) $K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$.

$\xrightarrow{\hspace{6cm}}$

Increasing order of deposition.

(b) Similarly the anion which is strogner reducing agent(low value of SRP) is liberated first at the anode.

$\xrightarrow[\text{Increasingorder of diposition}]{SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-}$

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FARADAY'S LAW OF ELECTROLYSIS :

First Law :

$w = zq$ $w = Z\,it$ Z = Electrochemical equivalent of substance

Second Law :

$W \alpha E$ $\frac{W}{E} = \text{constant}$ $\frac{W_1}{E_1} = \frac{W_2}{E_2} = ...$

$$\frac{W}{E} = \frac{i \times t \times \text{current efficiency factor}}{96500}.$$

CURRENT EFFICIENCY = $\frac{\text{actual mass deposited/produced}}{\text{Theoritical mass deposited/produced}} \times 100$

○ **CONDITION FOR SIMULTANEOUS DEPOSITION OF Cu & Fe AT CATHODE**

$$E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{Cu^{2+}} = E^o_{Fe^{2+}/Fe} - \frac{0.0591}{2}\log\frac{1}{Fe^{2+}}$$

Condition for the simultaneous deposition of Cu & Fe on cathode.

CONDUCTANCE :

☞ Conductance = $\frac{1}{\text{Resistance}}$

☞ **Specific conductance or conductivity :**

(Reciprocal of specific resistance) $K = \frac{1}{\rho}$ K = specific conductance

☞ **Equivalent conductance :**

$\lambda_E = \frac{K \times 1000}{\text{Normality}}$ unit : -ohm^{-1} cm^2 eq^{-1}

☞ **Molar conductance :**

$\lambda_m = \frac{K \times 1000}{\text{Molarity}}$ unit : -ohm^{-1} cm^2 mole^{-1}

specific conductance = conductance × $\frac{\ell}{a}$

KOHLRAUSCH'S LAW :

Variation of λ_{eq} / λ_M of a solution with concentration :

(i) Strong electrolyte

$$\lambda_M^c = \lambda_M^\infty - b\sqrt{c}$$

(ii) Weak electrolytes : $\lambda_\infty = n_+ \lambda^\infty_+ + n_- \lambda^\infty_-$ where λ is the molar conductivity

n_+ = No of cations obtained after dissociation per formula unit

n_- = No of anions obtained after dissociation per formula unit

APPLICATION OF KOHLRAUSCH LAW :

1. **Calculation of λ^0_M of weak electrolytes :**

$$\lambda^0_{M\,(CH_3COOH)} = \lambda^0_{M(CH_3COONa)} + \lambda^0_{M(HCl)} - \lambda^0_{M(NaCl)}$$

2. To calculate degree of diossociation of a week electrolyte

$$\alpha = \frac{\lambda^c_m}{\lambda^0_m} \qquad ; \qquad K_{eq} = \frac{c\alpha^2}{(1-\alpha)}$$

3. Solubility (S) of sparingly soluble salt & their K_{sp}

$$\lambda_M^{\,c} = \lambda_M^{\,\infty} = \kappa \times \frac{1000}{\text{solubility}}$$

$$K_{sp} = S^2.$$

❍ **IONIC MOBILITY :** It is the distance travelled by the ion per second under the potential gradient of 1 volts per cm. It's unit is $cm^2 s^{-1} v^{-1}$.

Absolute ionic mobility :

$$\lambda^0_c \propto \mu_c \qquad ; \qquad \lambda_a^{\,0} \propto \mu_a$$

$$\lambda^0_c = F\mu^0_c \qquad ; \qquad \lambda^0_a = F \times \mu^0_a.$$

$$\text{Ionic Mobility } \mu = \frac{v \xrightarrow{\quad} \text{speed}}{(V/\ell) \xrightarrow{\quad} \text{potential gradient}}$$

Transport Number :

$$t_c = \left[\frac{\mu_c}{\mu_c + \mu_a}\right], \qquad t_a = \left[\frac{\mu_a}{\mu_a + \mu_c}\right].$$

Where t_c = Transport Number of cation & t_a = Transport Number of anion

SOLUTION & COLLIGATIVE PROPERTIES

1.. **OSMOTIC PRESSURE :**

(i) $\pi = \rho gh$

Where, ρ = density of soln., h = equilibrium height.

(ii) **Vont – Hoff Formula** (For calculation of O.P.)

$$\pi = CST$$

$$\pi = CRT = \frac{n}{V}RT \text{ (just like ideal gas equation)}$$

$\therefore$ C = total conc. of all types of particles.

$$= C_1 + C_2 + C_3 + \ldots\ldots\ldots\ldots\ldots\ldots$$

$$= \frac{(n_1 + n_2 + n_3 + \ldots\ldots\ldots)}{V}$$

Note : If V_1 mL of C_1 conc. + V_2 mL of C_2 conc. are mixed.

$$\pi = \left(\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right)RT \qquad ; \qquad \pi = \left(\frac{\pi_1V_1 + \pi_2V_2}{RT}\right)$$

Type of solutions :

(a) Isotonic solution – Two solutions having same O.P.

$\pi_1 = \pi_2$ (at same temp.)

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(b) Hyper tonic– If $\pi_1 > \pi_2$. $\Rightarrow$ I^{st} solution is hypertonic solution w.r.t. 2^{nd} solution.

(c) Hypotonic – II^{nd} solution is hypotonic w.r.t. I^{st} solution.

Abnormal Colligative Properties : (In case of association or dissociation)

VANT HOFF CORRECTION FACTOR (i) :

$$i = \frac{\text{exp/observed/actual/abnormal value of colligative property}}{\text{Theoritical value of colligative property}}$$

$$= \frac{\text{exp./observed no. of particles / conc.}}{\text{Theoritical no. of particles}} = \frac{\text{observed molality}}{\text{Theoritical molality}}$$

$$= \frac{\text{theoretical molar mass (formula mass)}}{\text{experimental / observed molar mass (apparent molar mass)}}$$

- $i > 1 \Rightarrow$ dissociation.
  $i < 1 \Rightarrow$ association.

- $$i = \frac{\pi_{exp.}}{\pi_{theor}}$$

$\therefore \pi = iCRT$

$\pi = (i_1C_1 + i_2C_2 + i_3C_3.....)\ RT$

Relation between i & α (degree of dissociation) :

$$\mathbf{i = 1 + (n - 1)\alpha} \qquad \textbf{Where,} \qquad n = x + y.$$

Relation b/w degree of association β & i.

$$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

2. RELATIVE LOWERING OF VAPOUR PRESSURE (RLVP) **:**

Vapour pressure : $P_{Soln.} < P$

Lowering in VP $= P - P_s = \Delta P$

Relative lowering in vapour pressure $\text{RLVP} = \frac{\Delta P}{P}$

Raoult's law : – (For non – volatile solutes)

Experimentally relative lowering in V.P = mole fraction of the non volatile solute in solutions.

$$\text{RLVP} = \frac{P - P_s}{P} = X_{Solute} = \frac{n}{n + N}$$

$$\boxed{\frac{P - P_s}{P_s} = \frac{n}{N}}$$

$$\boxed{\frac{P - P_s}{P_s} = (\text{molality}) \times \frac{M}{1000}}$$ (M = molar mass of solvent)

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If solute gets associated or dissociated

$$\frac{P - P_s}{P_s} = \frac{i.n}{N}$$

$$\frac{P - P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$$

- According to Raoult's law
  (i) $p_1 = p_1^0 X_1$. where X_1 is the mole fraction of the solvent (liquid).
  (ii) An alternate form → $\frac{p_1^0 - p_1}{p_1^0} = X_2$.

- **Ostwald–Walker Method : Experimental or lab determination of $\frac{\Delta P}{P}$ or $\frac{\Delta P}{P_S}$**

$$\frac{P - P_s}{P_s} = \frac{\text{loss in wt. of solvent}}{\text{loss in wt. of solution}}$$

$$\frac{P - P_s}{P} = \frac{\text{loss in wt. of solvent}}{\text{gain in wt. of dehydrating agent}}$$

3. ELEVATION IN BOILING POINT :

$\Delta T_b = i \times K_b m$

$$K_b = \frac{RT_b^2}{1000 \times L_{vap}} \quad \text{or} \quad K_b = \frac{RT_b^2 M}{1000 \times \Delta H_{vap}}$$

$$L_{vap} = \left(\frac{\Delta H_{vap}}{M}\right)$$

4. DEPRESSION IN FREEZING POINT :

$\therefore \Delta T_f = i \times K_f . m.$

$$K_f = \text{molal depression constant} = \frac{RT_f^2}{1000 \times L_{fusion}} = \frac{RT_f^2 M}{1000 \times \Delta H_{fusion}}.$$

RAOULT'S LAW FOR BINARY (IDEAL) MIXTURE OF VOLATILE LIQUIDS :

$\mathbf{P_A = X_A P_A^0}$ $\therefore$ $\mathbf{P_B = X_B P_B^\circ}$

if $P_A^\circ > X_B^\circ$ $\therefore$ A is more volatile than B

$\therefore$ B.P. of A < B.P. of B

$\therefore$ According to Dalton's law

$\mathbf{P_T = P_A + P_B = X_A P_A^0 + X_B P_B^0}$

x_A' = mole fraction of A in vapour about the liquid / solution.

x_B' = mole fraction of B

$$\mathbf{P_A = X_A P_A^\circ = X_A' P_T}$$

$$\mathbf{P_B = X_B' P_T = X_B P_B^0}$$

$$\frac{1}{P_T} = \frac{x_A'}{P_A^0} + \frac{x_B'}{P_B^0}.$$

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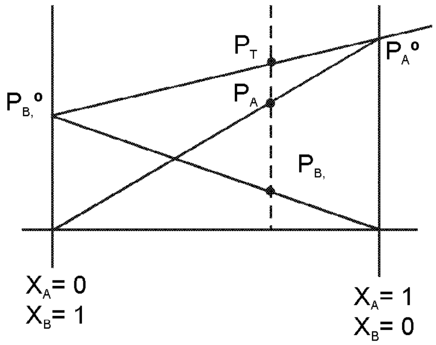
Graphical Representation :



A more volatile than B $(P_A{}^o > P_B{}^o)$

Ideal solutions (mixtures) : Mixtures which follow Raoul'ts law at all temperature.

A ------ A ⇒ A -------- B,
B ----- B

$\Delta H_{mix} = 0$: $\Delta V_{mix} = 0$: $\Delta S_{mix} = +$ ve as for process to proceed :$\Delta G_{mix} = -$ ve

eg. **(1) Benzene + Toluene.**
(2) Hexane + heptane.
(3) $C_2H_5Br + C_2H_5I$.

Non - Ideal solutions : Which do not obey Raoult's law.

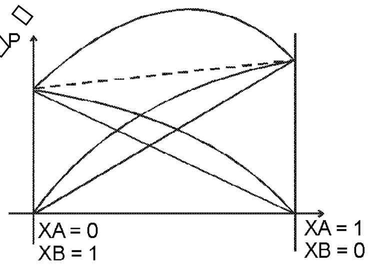
(a) Positive deviation : –

(i) $P_{T,exp} > (X_AP^o{}_A + X_BP_B{}^o)$

(ii) $\begin{matrix}A----A\\B----B\end{matrix} > A ---- B$
$\downarrow$
Weaker force of attraction

(iii) $\Delta H_{mix} = +ve$ energy absorbed
(iv) $\Delta V_{mix} = +ve$ (1L + 1L > 2L)
(v) $\Delta S_{mix} = +ve$
(vi) $\Delta G_{mix} = -ve$

eg. **$H_2O + CH_3OH$.**
$H_2O + C_2H_5OH$
C_2H_5OH + hexane
C_2H_5OH + cyclohexane.
$CHCl_3 + CCl_4 \rightarrow$ dipole dipole interaction becomes weak.



$P^0A > P^0B$

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(b) Negative deviation

(i) P_T exp $< x_A p^o + x_B p^o_B$

(ii) $\begin{matrix} A - - - - A \\ B - - - - B \end{matrix} > A \text{------} B.$

strong force of altraction.

(iii) $\Delta H_{mix} = -ve$

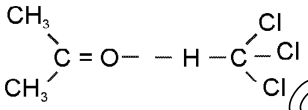
(iv) $\Delta V_{mix} = -ve$ (1L + 1L < 2L)

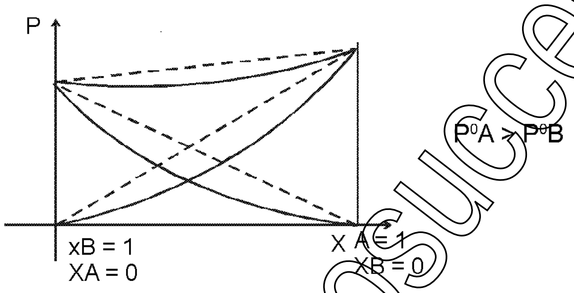
(v) $\Delta S_{mix} = +ve$

(vi) $\Delta G_{mix} = -ve$

eg. **$H_2O + HCOOH$**
$H_2O + CH_3COOH$
$H_2O + HNO_3$

$CHCl_3 + CH_3OCH_3$ ⇒





Immiscible Liquids :

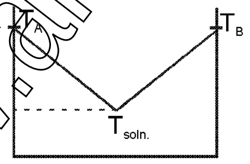
(i) $P_{total} = P_A + P_B$

(ii) $P_A = P_A{}^0 X_A = P_A{}^0$ [Since, $X_A = 1$].

(iii) $P_B = P_B{}^0 X_B = P_B{}^0$ [Since, $X_B = 1$].

(iv) $P_{total} = P_A{}^0 + P_B{}^0$ (v) $\frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$ (vi) $\frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$

$P_A{}^0 = \frac{n_A RT}{V}$; $P_B{}^0 = \frac{n_B RT}{V}$



B.P. of solution is less than the individual B.P.'s of both the liquids.

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Henry Law :

This law deals with dissolution of gas in liquid i.e. mass of any gas dissolved in any solvent per unit volume is proportional to pressure of gas in equilibrium with liquid.

$$m \propto p$$

$$m = kp$$

$$m \rightarrow \frac{\text{weight of gas}}{\text{Volume of liquid}}$$

SOLID STATE

❍ Classification of Crystal into Seven System

Crystal System	Unit Cell Dimensions and Angles	Bravais Lattices	Example
Cubic	$a = b = c\ ;\ \alpha = \beta = \gamma = 90°$	SC, BCC, FCC	NaCl
Orthorhombic	$a \neq b \neq c\ ;\ \alpha = \beta = \gamma = 90°$	SC, BCC, end centred & FCC	S_R
Tetragonal	$a = b \neq c\ ;\ \alpha = \beta = \gamma = 90°$	SC, BCC	Sn,ZnO_2
Monoclinic	$a \neq b \neq c\ ;\ \alpha = \gamma = 90° \neq \beta$	SC, end centred	S_M
Rhombohedral	$a = b = c\ ;\ \alpha = \beta = \gamma \neq 90°$	SC	Quartz
Triclinic	$a \neq b \neq c\ ;\ \alpha \neq \beta \neq \gamma \neq 90°$	SC	H_3BO_3
Hexagonal	$a = b \neq c\ ;\ \alpha = \beta = 90°\ ;\ \gamma = 120°$	SC	Graphite

❍ ANALYSIS OF CUBICAL SYSTEM

	Property	SC	BCC	FCC	
(i)	atomic radius (r)	$\frac{a}{2}$	$\frac{\sqrt{3}a}{4}$	$\frac{a}{2\sqrt{2}}$	a = edge length
(ii)	No. of atoms per unit cell (Z)	1	2	4	
(iii)	C.No.	6	8	12	
(iv)	Packing efficiency	52%	68%	74%	
(v)	No. voids				
	(a) octahedral (Z)	—	—	4	
	(b) Tetrahderal (2Z)	—	—	8	

❍ NEIGHBOUR HOOD OF A PARTICLE :

(I) Simple Cubic (SC) Structure :

Type of neighbour	Distance	no.of neighbours	
nearest	a	6	(shared by 4 cubes)
$(\text{next})^1$	$a\sqrt{2}$	12	(shared by 2 cubes)
$(\text{next})^2$	$a\sqrt{3}$	8	(unshared)

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(II) Body Centered Cubic (BCC) Structure :

Type of neighbour	Distance	no.of neighbours
nearest	$2r = a\frac{\sqrt{3}}{2}$	8
(next)^1	$= a$	6
(next)^2	$= a\sqrt{2}$	12
(next)^3	$= a\frac{\sqrt{11}}{2}$	24
(next)^4	$= a\sqrt{3}$	8

(III) Face Centered Cubic (FCC) Structure :

Type of neighbour	Distance	no. of neighbours
nearest	$\frac{a}{\sqrt{2}}$	$12 = \left(\frac{3\times 8}{2}\right)$
(next)^1	a	$6 = \left(\frac{3\times 8}{4}\right)$
(next)^2	$a\sqrt{\frac{3}{2}}$	24
(next)^3	$a\sqrt{2}$	12
(next)^4	$a\sqrt{\frac{5}{2}}$	24

- **DENSITY OF LATTICE MATTER (d)** $= \frac{Z}{N_A}\left(\frac{M}{a^3}\right)$

  where N_A = Avogadro's No. M = atomic mass or molecular mass.

- **IONIC CRYSTALS**

C.No.	Limiting radius ratio $\left(\frac{r_+}{r_-}\right)$
3	0.155 – 0.225 (Triangular)
4	0.225 – 0.414 (Tetrahedral)
6	0.414 – 0.732 (Octahedral)
8	0.732 – 0.999 (Cubic).

- **EXAMPLES OF A IONIC CRYSTAL**

  (a) Rock Salt (NaCl) Coordination number (6 : 6)

  (b) CsCl C.No. (8 : 8)

  Edge length of unit cell :-

  $a_{sc} = \frac{2}{\sqrt{3}}(r_+ + r_-)$

  (c) Zinc Blende (ZnS) C.No. (4 : 4)

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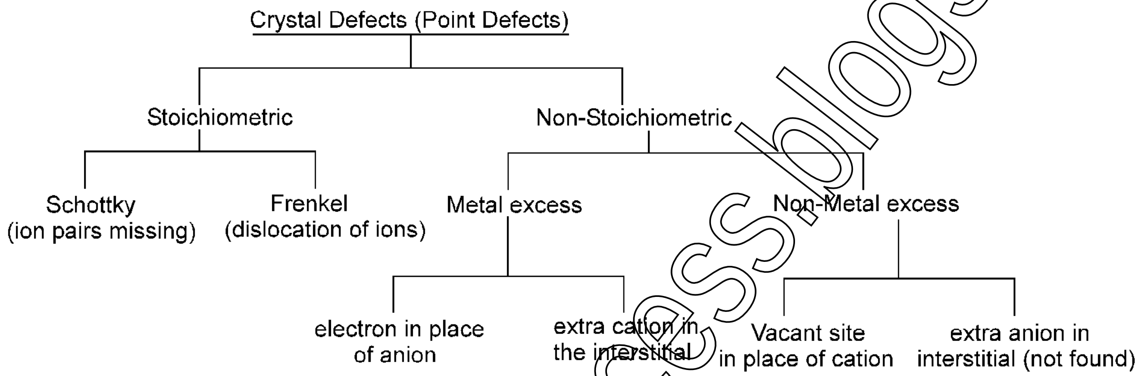
$$a_{fcc} = \frac{4}{\sqrt{3}} (r_{Zn^{2+}} + r_{s^{2-}})$$

(d) Fluorite structure (CaF_2) C.No. (8 : 4)

$$a_{fcc} = \frac{4}{\sqrt{3}} (r_{Ca^{2+}} + r_{F^-})$$

❍ Crystal Defects (Imperfections)



CHEMICAL KINETICS & REDIOACTIVITY

RATE/VELOCITY OF CHEMICAL REACTION :

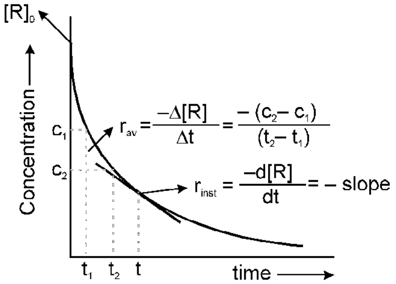
$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/lit.}}{\text{sec}} = \text{mol lit}^{-1}\text{ time}^{-1} = \text{mol dm}^{-3}\text{ time}^{-1}$$

Types of Rates of chemical reaction :

For a reaction $R \longrightarrow P$

$$\textbf{Average rate} = \frac{\text{Total change in concentration}}{\text{Total time taken}}$$

$$R_{\text{instantaneous}} = \lim_{t \to 0}\left[\frac{\Delta c}{\Delta t}\right] = \frac{dc}{dt} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$



RATE LAW (DEPENDENCE OF RATE ON CONCENTRATION OF REACTANTS) :

Rate = K (conc.)^{order} – differential rate equation or rate expression

Where K = Rate constant = specific reaction rate = rate of reaction when concentration is unity

unit of K = $(\text{conc})^{1-\text{order}}$ time^{-1}

Order of reaction :

$$m_1A + m_2B \longrightarrow \text{products.}$$

$R \propto [A]^p\,[B]^q$ Where p may or may not be equal to m_1 & similarly q may or may not be equal to m_2.

p is order of reaction with respect to reactant A and q is order of reaction with respect to reactant B and (p + q) is **overall order of the reaction.**

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INTEGRATED RATE LAWS :

C_0 or 'a' is initial concentration and C_t or a – x is concentration at time 't'

(a) zero order reactions :

Rate = k [conc.]° = constant

Rate = k = $\dfrac{C_0 - C_t}{'t'}$ or $C_t = C_0 - kt$

Unit of K = mol lit^{-1} sec^{-1}, Time for completion = $\dfrac{C_0}{k}$

at $t_{1/2}$, C_t = $\dfrac{C_0}{2}$, so $kt_{1/2} = \dfrac{C_0}{2}$ ⇒ $\mathbf{t_{1/2}} = \dfrac{C_0}{2k}$ $\therefore t_{1/2} \propto C_0$

(b) First Order Reactions :

(i) Let a 1st order reaction is, $A \longrightarrow$ Products

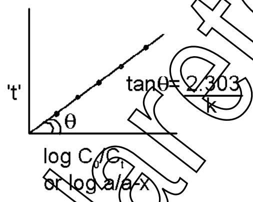
$\mathbf{t} = \dfrac{2.303}{k}\ \mathbf{log}\ \dfrac{a}{a-x}$ or $k = \dfrac{2.303}{t} \log \dfrac{C_0}{C_t}$

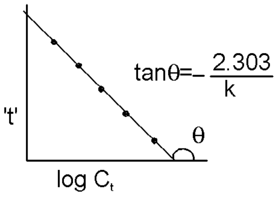
⇒ $t_{1/2} = \dfrac{\ell n2}{\mathbf{k}} = \dfrac{0.693}{\mathbf{k}}$ = Independent of initial concentration.

$t_{Avg.} = \dfrac{1}{k} = 1.44\ t_{1/2}$.

Graphical Representation :

$t = -\dfrac{2.303}{k} \log C_t + \dfrac{2.303}{R} \log C_0$





(c) Second order reaction :

2nd order Reactions
Two types

$A + A \longrightarrow$ products
a a
(a – x) (a – x)

$\therefore \dfrac{dx}{dt} = k(a-x)^2$

$\Rightarrow \dfrac{1}{(a-x)} - \dfrac{1}{a} = \mathbf{kt}$

$A + B \longrightarrow$ products.
a b 0
a – x b – x

$\dfrac{dx}{dt} = k(a-x)(b-x)$

$\mathbf{k} = \dfrac{2.303}{t(a-b)}\ \mathbf{log}\ \dfrac{b(a-x)}{a(b-x)}$

(d) Psuedo first order reaction :

$\therefore$ For $A + B \longrightarrow$ Products [Rate = K $[A]^1$ $[B]^1$]

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Now if 'B' is taken in large excess b > > a.

$$\Rightarrow \quad k = \frac{2.303}{bt} \log \frac{a}{a-x}$$

$\because$ 'b' is very large can be taken as constant

$\Rightarrow kb = \frac{2.303}{t} \log \frac{a}{a-x}$ $\Rightarrow$ $k' = \frac{2.303}{t} \log \frac{a}{a-x}$, k′ is psuedo first order rate constant

METHODS TO DETERMINE ORDER OF A REACTION

(a) Initial rate method :

$r = k\,[A]^a\,[B]^b\,[C]^c$ if $[B]$ = constant

$[C]$ = constant

then for two different initial concentrations of A we have

$$r_{0_1} = k\,[A_0]_1^{\,a} \;,\; r_{0_2} = k\,[A_0]_2^{\,a} \quad \Rightarrow \quad \frac{r_{0_1}}{r_{0_2}} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^a$$

(b) Using integrated rate law : It is method of trial and error.

(c) Method of half lives :

for n^{th} order reaction $t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$

(d) Ostwald Isolation Method :

rate = $k\,[A]^a\,[B]^b\,[C]^c = k_0\,[A]^a$

METHODS TO MONITOR THE PROGRESS OF THE REACTION :

(a) Progress of gaseous reaction can be monitored by measuring total pressure at a fixed volume & temperature or by measuring total volume of mixture under constant pressure and temperature. $\therefore$ **k =** $\frac{2.303}{t}$ **log** $\frac{P_0(n-1)}{nP_0 - P_t}$ {Formula is not applicable when n = 1, the value of n can be fractional also.}

(b) By titration method :

1. $\therefore \; a \propto V_0 \qquad a - x \propto V_t \qquad \Rightarrow \qquad k = \frac{2.303}{t} \log \frac{V_0}{V_t}$

2. Study of acid hydrolysis of an easter.

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

(c) By measuring optical rotation produced by the reaction mixture :

$$k = \frac{2.303}{t} \log \left(\frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}\right)$$

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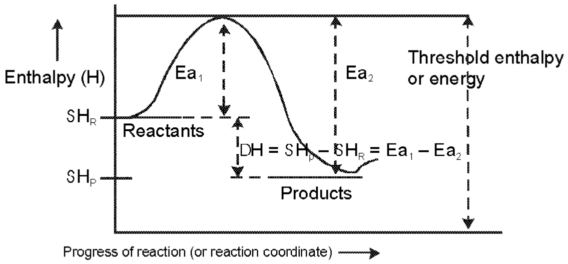
EFFECT OF TEMPERATURE ON RATE OF REACTION.

$$\text{T.C.} = \frac{K_t + 10}{K_t} \approx 2 \text{ to } 3 \text{ (for most of the reactions)}$$

Arhenius theroy of reaction rate.



SH_R = Summation of enthalpies of reactants
SH_P = Summation of enthalpies of reactants
DH = Enthalpy change during the reaction
Ea_1 = Energy of activation of the forward reaction
Ea_2 = Energy of activation of the backward reaction

$E_P > E_r \longrightarrow$ endothermic
$E_P < E_r \longrightarrow$ exothermic

$$\Delta H = (E_P - E_r) = \text{enthalpy change}$$

$$\Delta H = E_{af} - E_{ab}$$

$$E_{threshold} = E_{af} + E_r = E_b + E_p$$

Arhenius equation

$$k = Ae^{-E_a RT}$$

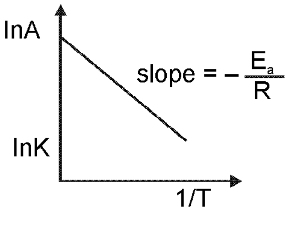
$$r = k\,[\text{conc.}]^{order}$$

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$$

$$\log k = \left(-\frac{Ea}{2.303\ R} \right)\frac{1}{T} + \log A$$

If k_1 and k_2 be the rate constant of a reaction at two different temperature T_1 and T_2 respectively, then we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$



- ❖ $\ln k = \ln A - \frac{E_a}{RT}$

- ❖ $T \to \infty,\ K \to A.$

$E_a \geq O$

REVERSIBLE REACTIONS

$$k_f = A_f\ e^{-E_{af}/RT}$$

$$k_b = A_b\ e^{-E_{ab}/RT}$$

$$K_{eq} = \frac{K_f}{K_b} = \left(\frac{A_f}{A_b} \right) e^{-(E_{af} - E_{ab})/RT}$$

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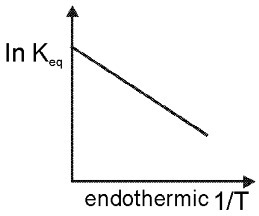
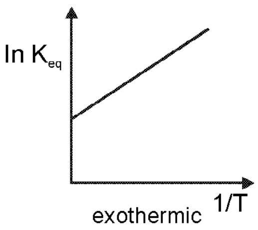
$$\ln K_{eq} = -\frac{\Delta H}{RT} + \ln\left(\frac{A_f}{A_b}\right)$$





$$\frac{[B]}{[C]} = \frac{K_1}{K_2} \qquad \Rightarrow \qquad E_a = \frac{E_{a_1}k_1 + E_{a_2}k_2}{k_1 + k_2}$$

(ii) REVERSIBLE 1ST ORDER REACATION (both forward and backward)

$$\boxed{x = \frac{K_f a}{K_f + K_b}\left(1 - e^{-(k_f + k_b)t}\right)}$$

$$\boxed{K_f + K_b = \frac{1}{t}\ln\left(\frac{x_{eq.}}{x_{eq.} - x}\right)}$$

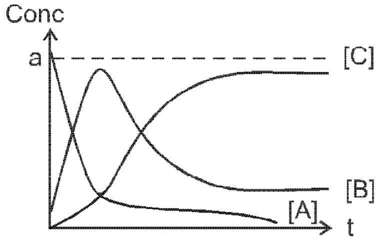
(iii) SEQUENTIAL 1ST ORDER REACTION

$[A] = [A]\,e^{-k_1 t}$

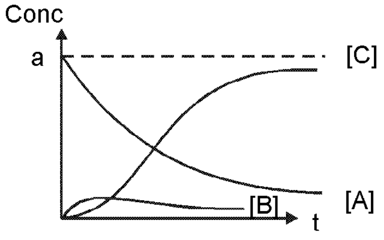
$x = a(1 - e^{-k_1 t})$

$$\boxed{y = \frac{K_1 a}{K_2 - K_1}\{e^{-k_1 t} - e^{-k_2 t}\}} \qquad t_{B(max.)} = \frac{1}{(K_1 - K_2)}\ln\frac{K_1}{K_2}$$

CASE-I $K_1 >> K_2$



CASE II : $K_2 >> K_1$



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INORGANIC

PERIODIC TABLE & PERIODICITY

Development of Modern Periodic Table :

(a) Dobereiner's Triads : He arranged similar elements in the groups of three elements called as triads

(b) Newland's Law of Octave : He was the first to correlate the chemical properties of the elements with their atomic masses.

(c) Lother Meyer's Classification : He plotted a graph between atomic masses against their respective atomic volumes for a number of elements. He found the observations ; **(i)** elements with similar properties occupied similar positions on the curve, **(ii)** alkali metals having larger atomic volumes occupied the crests, **(iii)** transitions elements occupied the troughs, **(iv)** the halogens occupied the ascending portions of the curve before the inert gases and

(v) alkaline earth metals occupied the positions at about the mid points of the descending portions of the curve. On the basis of these observations he concluded that the atomic volumes (a physical property) of the elements are the periodic functions of their atomic masses.

(d) Mendeleev's Periodic Table :

Mendeleev's Periodic's Law

the physical and chemical properties of the elements are the periodic functions of their atomic masses.

Periods	Number of Elements	Called as
$(1)^{st}$ n = 1	2	Very short period
$(2)^{nd}$ n = 2	8	Short period
$(3)^{rd}$ n = 3	8	Short period
$(4)^{th}$ n = 4	18	Long period
$(5)^{th}$ n = 5	18	Long period
$(6)^{th}$ n = 6	32	Very long period
$(7)^{th}$ n = 7	19	Incomplete period

Merits of Mendeleev's Periodic table:

- It has simplified and systematised the study of elements and their compounds.
- It has helped in predicting the discovery of new elements on the basis of the blank spaces given in its periodic table.

Demerits in Mendeleev's Periodic Table :

- Position of hydrogen is uncertain .It has been placed in IA and VIIA groups
- No separate positions were given to isotopes.
- Anomalous positions of lanthanides and actinides in periodic table.
- Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table.
- Similar elements were placed in different groups.
- It didn't explained the cause of periodicity.

(e) Long form of the Periodic Table or Moseley's Periodic Table :

Modern Periodic Law (Moseley's Periodic Law) :

If the elements are arranged in order of their increasing atomic number, after a regular interval, elements with similar properties are repeated.

Periodicity :

The repetition of the properties of elements after regular intervals when the elements are arranged in the order of increasing atomic number is called periodicity.

Cause of Periodicity :

The periodic repetition of the properties of the elements is due to the recurrence of similar valence shell electronic configurations after certain regular intervals.
The modern periodic table consists of horizontal rows (periods) and vertical column (groups).

Periods :
There are seven periods numbered as 1, 2, 3, 4, 5, 6 and 7.

- Each period consists of a series of elements having same valence shell.
- Each period corresponds to a particular principal quantum number of the valence shell present in it.
- Each period starts with an alkali metal having outermost electronic configuration as ns^1.
- Each period ends with a noble gas with outermost electronic configuration ns^2np^6 except helium having outermost electronic configuration as $1s^2$.
- Each period starts with the filling of new energy level.
- The number of elements in each period is twice the number of atomic orbitals available in energy level that is being filled.

Groups :
There are eighteen groups numbered as 1, 2, 3, 4, 5, ... 13, 14, 15, 16, 17, 18.
Group consists of a series of elements having similar valence shell electronic configuration.

S–Block Elements

d –Block Elements

p–Block Elements

1 IA	2 II A	3 III B	4 IV B	5 V B	6 VI B	7 VII B	8 VIII	9 VIII	10 VIII	11 I B	12 II B	13 III A	14 IV A	15 V A	16 VI A	17 VII A	18 VIII A
1 H 1.007																	2 He 4.002
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.006	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.98	12 Mg 24.30											13 Al 26.981	14 Si 28.085	15 P 30.973	16 S 32.006	17 Cl 35.452	18 Ar 39.948
19 K 39.08	20 Ca 40.078	21 Sc 44.959	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.938	26 Fe 55.84	27 Co 55.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.921	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.46	38 Sr 87.62	39 Y 88.905	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 102.905	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.904	54 Xe 132.29
55 Cs 132.90	56 Ba 137.27	57 La* 138.905	72 Hf 178.49	73 Ta 180.947	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.666	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 207.980	84 Po 209	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226	89 Ac** 227	104 Rf 261.11	105 Ha 262.114	106 Sg 263.118	107 Bh 262.12	108 Hs 265	109 Mt 266	110 Uun 269				114 Uuq				

Inner - Transition Metals (f-Block elements)

***Lanthanides**	58 Ce 140.115	59 Pr 140.907	60 Nd 144.24	61 Pm 145	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
****Actinides**	90 Th 232.038	91 Pa 231	92 U 238.028	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260

Classification of the Elements :

(a) s-block elements

Group 1 & 2 elements constitute the s-block. General electronic configuration is [inert gas] ns^{1-2}
s-block elements lie on the extreme left of the periodic table.

(b) p-block elements

Group 13 to 18 elements constitute the p-block. General electronic configuration is [inert gas] ns^2np^{1-6}

(c) d-Block elements

Group 3 to 12 elements constitute the d-block. General electronic configuration is [inert gas] (n – 1) d^{1-10} ns^{1-2}

(d) f-Block elements

General electronic configuration is (n – 2) f^{1-14} (n – 1) d^{0-1} ns^2. All f-block elements belong to 3rd group.

Elements of f-blocks have been classified into two series. **(1)** Ist inner transition or 4 f-series, contains 14 elements $_{58}$Ce to $_{71}$Lu. **(2).** IInd inner transition or 5 f-series, contains 14 elements $_{90}$Th to $_{103}$Lr.

Prediction of period, group and block :

- ❍ Period of an element corresponds to the principal quantum number of the valence shell.
- ❍ The block of an element corresponds to the type of subshell which receives the last electron.
- ❍ The group is predicted from the number of electrons in the valence shell or/and penultimate shell as follows.

(a) For s-block elements ; Group no. = the no. of valence electrons
(b) For p-block elements ; Group no. = 10 + no. of valence electrons
(c) For d-block elements ; Group no. = no. of electrons in (n – 1) d sub shell + no. of electrons in valence shell.

Metals and nonmetals :

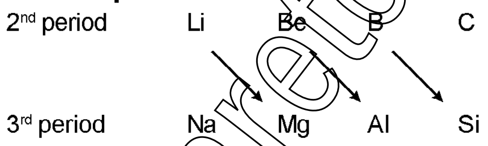
♦ The metals are characterised by their nature of readily giving up the electron(s) and from shinning lustre. Metals comprises more than 78% of all known elements and appear on the left hand side of the periodic table. Metals are usually solids at room temperature (except mercury, gallium). They have high melting and boiling points and are good conductors of heat and electricity. Oxides of metals are generally basic in nature (some metals in their higher oxidation state form acid oxides e.g. CrO_3).

♦ Nonmetals do not lose electrons but take up electrons to form corresponding anions. Nonmetals are located at the top right hand side of the periodic table. Nonmetals are usually solids, liquids or gases at room temperature with low melting and boiling points. They are poor conductors of heat and electricity. Oxides of nonmetals are generally acidic in nature.

Metalloids (Semi metals) :

The metalloids comprise of the elements B, Si, Ge, As, Sb and Te.

Diagonal relationship :



Diagonal relationship arises because of ;

(i) on descending a group, the atoms and ions increase in size. On moving from left to right in the periodic table, the size decreases. Thus on moving diagonally, the size remains nearly the same.

(Li = 1.23 Å & Mg = 1.36 Å ; Li^+ = 0.76 Å & Mg^{2+} = 0.72 Å)

(ii) it is sometimes suggested that the diagonal relationship arises because of diagonal similarity in electronegativity values.

(Li = 1.0 & Mg = 1.2 ; Be = 1.5 & Al = 1.5 ; B = 2.0 & Si = 1.8)

The periodicity of atomic properties :

(i) Effective nuclear charge :

The effective nuclear charge (Z_{eff}) = Z – σ, (where Z is the actual nuclear charge (atomic number of the element) and σ is the shielding (screening) constant). The value of σ i.e. shielding effect can be determined using the Slater's rules.

(ii) Atomic radius :

(A) Covalent radius : It is one-half of the distance between the centres of two nuclei (of like atoms) bonded by a single covalent bond. Covalent radius is generally used for nonmetals.

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(B) **Vander Waal's radius (Collision radius) :** It is one-half of the internuclear distance between two adjacent atoms in two nearest neighbouring molecules of the substance in solid state.

(C) **Metallic radius (Crystal radius) :**
It is one-half of the distance between the nuclei of two adjacent metal atoms in the metallic crystal lattice.

♦ Thus, the covalent, vander Wall's and metallic radius magnitude wise follows the order,

$$r_{\text{covalent}} < r_{\text{crystal}} < r_{\text{vander Walls}}$$

Variation in a Period	**Variation in a Group**
In a period left to right :	In a group top to bottom :
Nuclear charge (Z) increases by one unit	Nuclear charge (Z) increases by more than one unit
Effective nuclear charge (Z_{eff}) also increases	Effective nuclear charge (Z_{eff}) almost remains constant because of increased screening effect of inner shells electrons.
But number of orbitals (n) remains constant	But number of orbitals (n) increases
As a result, the electrons are pulled closer to the nucleus by the increased Z_{eff}. $r_n \propto \frac{1}{Z^*}$ Hence atomic radii decrease with increase in atomic number in a period from left to right.	The effect of increased number of atomic shells overweighs the effect of increased nuclear charge. As a result of this the size of atom increases from top to bottom in a given group.

(iii) **Ionic radius :**

The effective distance from the centre of nucleus of the ion up to which it has an influence in the ionic bond is called ionic radius.

Cation	**Anion**
It is formed by the lose of one or more electrons from the valence shell of an atom of an element. Cations are smaller than the parent atoms because, (i) the whole of the outer shell of electrons is usually removed. (ii) in a cation, the number of positive charges on the nucleus is greater than number of orbital electrons leading to incresed inward pull of remaining electrons causing contraction in size of the ion.	It is formed by the gain of one or more electrons in the valence shell of an atom of an element. Anions are larger than the parent atoms because (i) anion is formed by gain of one or more electrons in the neutral atom and thus number of electrons increases but magnitude of nuclear charge remains the same. (ii) nuclear charge per electrons is thus reduced and the electrons cloud is held less tightly by the nucleus leading to the expansion of the outer shell. Thus size of anion is increased.

(iv) **Ionisation Energy :**

Ionisation energy (IE) is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form a cation.

$$M(g) \xrightarrow{(IE_1)} M^+(g) + e^- \quad ; \quad M^+(g) + IE_2 \longrightarrow M^{2+}(g) + e^-$$

$$M^{2+}(g) + IE_3 \longrightarrow M^{+3}(g) + e^-$$

IE_1, IE_2 & IE_3 are the Ist, IInd & IIIrd ionization energies to remove electron from a neutral atom, monovalent and divalent cations respectively. In general, $(IE)_1 < (IE)_2 < (IE)_3 < \ldots\ldots\ldots\ldots$

♦ **Factors Influencing Ionisation energy**

(A) **Size of the Atom :** Ionisation energy decreases with increase in atomic size.

(B) **Nuclear Charge :** The ionisation energy increases with increase in the nuclear charge.

(C) **Shielding or screening effect :** The larger the number of electrons in the inner shells, greater is the screening effect and smaller the force of attraction and thus ionization energy (IE) decreases.

(D) **Penetration effect of the electron :** Penetration effect of the electrons follows the order s > p > d > f for, the same energy level. Higher the penetration of electron higher will be the ionisation energy.

(E) **Electronic Configuration :** If an atom has exactly half-filled or completely filled orbitals, then such an arrangement has extra stability.

(V) **Electron Gain Enthalphy : (CHANGED TOPIC NAME)**

The electron gain enthalpy $\Delta_{eg}H^{\ominus}$, is the change in standard molar enthalpy when a neutral gaseous atom gains an electron to form an anion.

$$X(g) + e^-(g) \longrightarrow X^-(g)$$

The second electron gain enthalpy, the enthalpy change for the addition of a second electron to an initially neutral atom, invariably positive because the electron repulsion out weighs the nuclear attraction.

- Group 17 elements (halogens) have very high negative electron gain enthalpies (i.e. high electron affinity) because they can attain stable noble gas electronic configuration by picking up an electron.
- Across a period, with increase in atomic number, electron gain enthalpy becomes more negative
- As we move in a group from top to bottom, electron gain enthalpy becomes less negative
- Noble gases have large positive electron gain enthalpies
- Negative electron gain enthalpy of O or F is less than S or Cl.
- Electron gain enthalpies of alkaline earth metals are very less or positive
- Nitrogen has very low electron affinity
- (i) Electron affinity $\propto \frac{1}{\text{Atomic size}}$ (ii) Electron affinity $\propto$ Effective nuclear charge (z_{eff})

  (iii) Electron affinity $\propto \frac{1}{\text{Screening effect}}$. (iv) Stability of half filled and completely filled orbitals of a subshell is comparatively more and the addition of an extra electron to such an system is difficult and hence the electron affinity value decreases.

(VI) Electronegativity :

Electronegativity is a measure of the tendency of an element to attract shared electrons towards itself in a covalently bonded molecules.

(a) **Pauling's scale :**

$$\Delta = X_A - X_B = 0.208\sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

E_{A-B} = Bond enthalpy/ Bond energy of A – B bond.
E_{A-A} = Bond energy of A – A bond
E_{B-B} = Bond energy of B – B bond

(All bond energies are in kcal / mol)

$$\Delta = X_A - X_B = 0.1017\sqrt{E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

All bond energies are in kJ / mol.

(b) **Mulliken's scale :**

$$\chi_M = \frac{IE + EA}{2}$$

Paulings's electronegativity χ_P is related to Mulliken's electronegativity χ_M as given below.

$$\chi_P = 1.35\,(\chi_M)^{1/2} - 1.37$$

Mulliken's values were about 2.8 times larger than the Pauling's values.

(VII) Periodicity of Valence or Oxidation States :

There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids.

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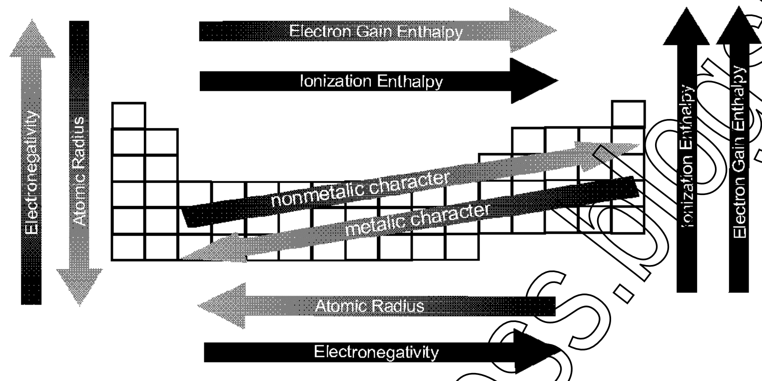
(VIII) Periodic Trends and Chemical Reactivity :

- In a group, basic nature of oxides increases or acidic nature decreases. Oxides of the metals are generally basic and oxides of the nonmetals are acidic. The oxides of the metalloids are generally amphoteric in nature. The oxides of Be, Al, Zn, Sn, As, Pb and Sb are amphoteric.
- In a period the nature of the oxides varies from basic to acidic.

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Strongly basic	Basic	amphoteric	Weakly acidic	Acidic	Acidic	Strongly acidic



CHEMICAL BONDING

Chemical Bond :

In the process each atom attains a stable outer electronic configuration of inert gases.

Ionic or Electrovalent Bond :

The formation of an ionic compound would primarily depends upon :

* The ease of formation of the positive and negative ions from the respective neutral atoms.

* The arrangement of the positive and negative ions in the solid, that is the lattice of the crystalline compound.

Conditions for the formation of ionic compounds :

(i) Electronegativity difference between two combining elements must be larger.

(ii) Ionization enthalpy ($M(g) \rightarrow M^+(g) + e^-$) of electropositive element must be low.

(iii) Negative value of electron gain enthalpy ($X(g) + e^- \rightarrow X^-(g)$) of electronegative element should be high.

(iv) Lattice enthalpy ($M^+(g) + X^-(g) \rightarrow MX(s)$) of an ionic solid must be high.

Lattice Enthalpy :

The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

Factors affecting lattice energy of an ionic compound :

(i) Lattice energy $\propto \frac{1}{r_+ + r_-}$ where $(r_+ + r_-)$ = Inter-ionic Distance.

(ii) Lattice energy $\propto Z_+, Z_-$

$Z_+ \Rightarrow$ charge on cation in terms electronic charge.

$Z_- \Rightarrow$ charge on anion in terms electronic charge.

Determination of lattice energy :

Born-Haber Cycle :

It inter relates the various energy terms involved during formation of an ionic compound.

It a thermochemical cycle based on the Hess's law of constant heat summation.

Hydration :

All the simple salts dissolve in water, producing ions, and consequently the solution conduct electricity. Since Li^+ is very small, it is heavily hydrated. This makes radius of hydrated Li^+ ion large and hence it moves only slowly. In contrast, Cs^+ is the least hydrated because of its bigger size and thus the radius of the Cs^+ ion is smaller than the radius of hydrated Li^+, and hence hydrated Cs^+ moves faster, and conducts electricity more readily.

Hydrolysis :

Hydrolysis means reaction with water molecules ultimately leading to breaking of O-H bond into H^+ and OH^- ions.

Hydrolysis in covalent compounds takes place generally by two mechanisms
(a) By Coordinate bond formation : Generally in halides of atoms having vacant d-orbitals or of halides of atoms having vacant orbitals.
(b) By H-bond formation : For example in Nitrogen trihalides

General properties of ionic compounds :

(a) **Physical state :** At room temperature ionic compounds exist either in solid state or in solution phase but not in gaseous state.

(b) Simple ionic compounds do not show isomerism but isomorphism is their important characteristic.
e.g. , $FeSO_4 . 7H_2O$ | $MgSO_4 . 7H_2O$

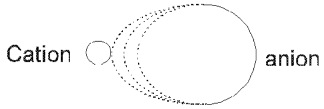
(c) **Electrical conductivity :**
All ionic solids are good conductors in molten state as well as in their aqueous solutions because their ions are free to move.

(D) SOLUBILITY OF IONIC COMPOUNDS :

Soluble in polar solvents like water which have high dielectric constant

Covalent character in ionic compounds (Fajan's rule) :

Fajan's pointed out that greater is the polarization of anion in a molecule, more is covalent character in it.



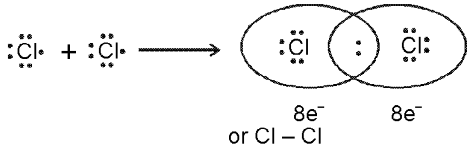
More distortion of anion, more will be polarisation then covalent character increases.

Fajan's gives some rules which govern the covalent character in the ionic compounds, which are as follows:

(i) **Size of cation : Size of cation α 1 / polarisation.**
(ii) **Size of anion : Size of anion α polarisation**
(iii) **Charge on cation : Charge on cation α polarisation.**
(iv) **Charge on anion : Charge on anion α polarisation.**
(v) **Pseudo inert gas configuration of cation :**

Covalent Bond :

It forms by sharing of valence electrons between atoms to form molecules e.g., formation of Cl_2 molecule :



Covalent bond between two Cl atoms

The important conditions being that :
(i) Each bond Is formed as a result of sharing of an electron pair between the atoms.
(ii) Each combining atom contributes at least one electron to the shared pair.
(iii) The combining atoms attain the outer- shell noble gas configurations as a result of the sharing of electrons.

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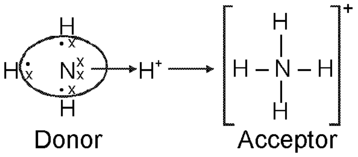
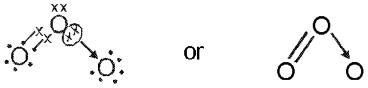
Coordinate Bond (Dative Bond):

The bond formed between two atom in which contribution of an electron pair is made by one of them while the sharing is done by both.

(i) NH_4^+ (ammonium ion)



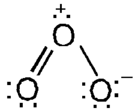
(ii) O_3 (ozone)



Other examples : H_2SO_4 , HNO_3 , H_3O^+ , N_2O, $[Cu(NH_3)_4]^{2+}$

Formal Charge :

Formal charge (F.C.) On an atom in a Lewis structure = [Total number of valence electron in the free atom] – [Total number of non bonding (lone pair) electrons] – (½) [Total number of bonding (shared) electrons]



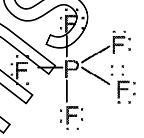
Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.

Limitations of the Octet Rule :

1. **The incomplete octet of the central atom**
   LiCl, BeH_2 and BCl_3, $AlCl_3$ and BF_3

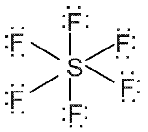
2. **Odd-electron molecules**
   nitric oxide, NO and nitrogen dioxide. NO_2

3. **The expanded octet**



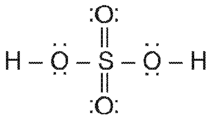
PF_5

10 electrons around the P atom



SF_6

12 electrons around the S atom



H_2SO_4

12 electrons around the S atom

4. **Other drawbacks of the octet theory**

(i) some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2 , KrF_2 , $XeOF_2$ etc.,

(ii) This theory does not account for the shape of molecules.

(iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

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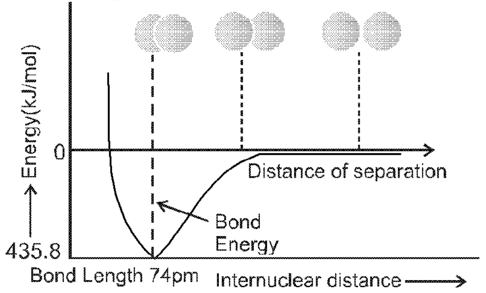
Valence bond theory (VBT) :

$H_2(g) + 435.8\ kJ\ mol^{-} \rightarrow H(g) + H(g)$



Orbital Overlap Concept

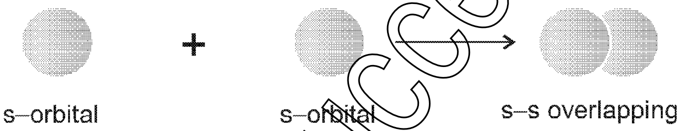
according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present, in the valence shell having opposite spins.

Types of Overlapping and Nature of Covalent Bonds

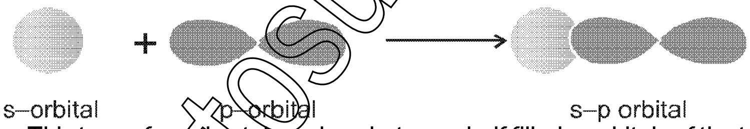
The covalent bond may be classified into two types depending upon the types of overlapping :
(i) sigma(σ) bond, and (ii) pi (π) bond

(i) **Sigma (σ) bond :** This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis.

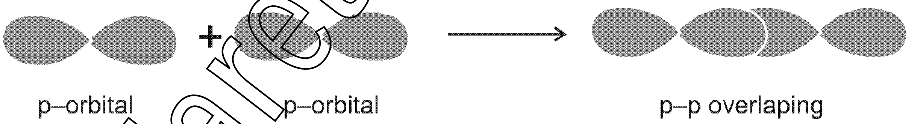
- s-s overlapping



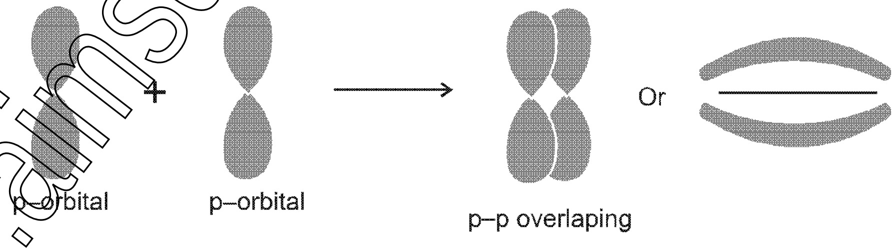
- s-p overlapping:



- p-p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms.



(ii) **pi(π) bond :** In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis.



Strength of Sigma and pi Bonds :

In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent.

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Valence shell electron pair repulsion (VSEPR) theory :

The main postulates of VSEPR theory are as follows:

(i) The shape of a molecule depends upon the number of valence shell electron pairs [bonded or nonbonded) around the central atom.

(ii) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

(iii) These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.

(iv) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

(v) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

(vi) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pairs decreases in the order :
lone pair (ℓp) - lone pair (ℓp) > lone pair (ℓp) - bond pair (bp) > bond pair (bp) -bond pair (bp)

Hybridisation :

Salient features of hybridisation :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.

2. The hybridised orbitals are always equivalent in energy and shape.

3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement is obtained. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation :

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is the orbital that undergo hybridization and not the electrons.

Determination of hybridisation of an atom in a molecule or ion:

Steric number rule (given by Gillespie) :

Steric No. of an atom = number of atom bonded with that atom + number of lone pair(s) left on that atom.

Table-3

Steric number	**Types of Hybridisation**	**Geometry**
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
7	sp^3d^3	Pentagonal bipyramidal

Hybridization Involving d-orbital :

Type of 'd' orbital involved

sp^3d	dz^2
sp^3d^2	$dx^2 - y^2$ & dz^2
sp^3d^3	$dx^2 - y^2$, dz^2 & dxy
dsp^2	$d_{x^2-y^2}$

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Molecular Orbital Theory (MOT) :

developed by F. Hund and R.S. Mulliken in 1932.

(i) Molecular orbitals are formed by the combination of atomic orbitals of comparable energies and proper symmetry.

(ii) An electron in an atomic orbital is influenced by one nucleus, while in a molecular orbital it is influenced by two or more nuclei depending upon the number of the atoms in the molecule. **Thus an atomic orbital is monocentric while a molecular orbital is polycentric.**

(iii) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals called **bonding molecular orbital** and **anti-bonding molecular orbital** are formed.

(iv) The molecular orbitals like the atomic orbitals are filled in accordance with the **Aufbau principle** obeying the **Pauli Exclusion principle** and the **Hund's Rule of Maximum Multiplicity**. But the filling order of these molecular orbitals is always **experimentally decided**, there is no rule like (n + l) rule in case of atomic orbitals.

CONDITIONS FOR THE COMBINATION OF ATOMIC ORBITALS :

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS :

The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

The important characteristic feature of this order is that the **energy of $\sigma 2p_z$ molecular orbital is higher than that of $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals.**

BOND ORDER

Bond order (b.o.) = ½ ($N_b - N_a$)

A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

NATURE OF THE BOND :

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

BOND-LENGTH :

The bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

MAGNETIC NATURE :

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field) e.g., N_2 molecule.

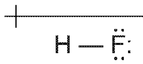
Dipole moment :

Dipole moment (μ) = Magnitude of charge (q) × distance of separation (d)

Dipole moment is usually expressed in Debye units (D). The conversion factors are

- 1 D = 3.33564 × 10^{-30} Cm, where C is coulomb and m is meter.
- 1 Debye = 1 × 10^{-18} e.s.u. cm.

For example the dipole moment of HF may be represented as



The shift in electron density is represented by crossed arrow (⟼) above the Lewis structure to indicate the direction of the shift.

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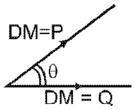
a molecule will have a dipole moment if the summation of all of the individual moment vector is non-zero.

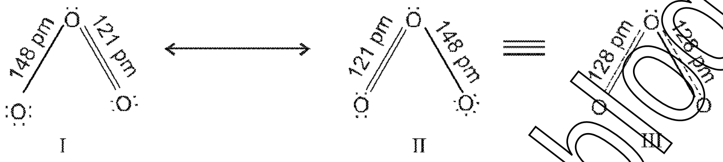


$R = \sqrt{P^2 + Q^2 + 2PQ\cos\theta}$, where R is resultant dipole moment.

Resonance :

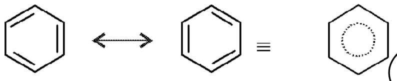
Definition : Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound.

For example, the ozone, O_2 molecule can be equally represented by the structures I and II shown below :



Resonance in the O_3 molecule

Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



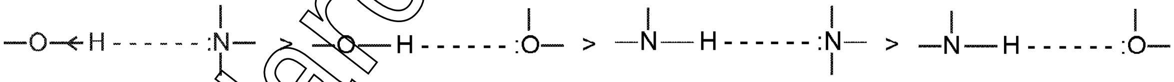
Resonance hybrid

Hydrogen Bond :

$$---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}---H^{\delta+}-F^{\delta-}$$

Conditions required for H-bond :
(i) Molecule should have more electronegative atom (F, O, N) linked to H-atom.
(ii) Size of electronegative atom should be smaller.
(iii) A lone pair should be present on electronegative atom.

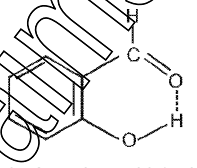
- Order of H-bond strength



$$-O-H------:\overset{|}{\underset{|}{N}}- \;>\; -O-H------:\overset{|}{O}- \;>\; -\overset{|}{N}-H------:\overset{|}{\underset{|}{N}}- \;>\; -\overset{|}{N}-H------:\overset{|}{O}-$$

TYPES OF H-BONDS :

(A) Intramolecular H-Bonding :
it is formed when hydrogen atom is present in between the two highly electronegative (F, O, N) atoms within the same molecule.



o-hydroxy benzaldehyde

It has lower boiling point (i.e. more volatile) than its para-derivative

Necessary conditions for the formation of intramolecular hydrogen-bonding :
(a) the ring formed as a result of hydrogen bonding should be planar.
(b) a 5- or 6- membered ring should be formed.
(c) interacting atoms should be placed in such a way that there is minimum strain during the ring closure.

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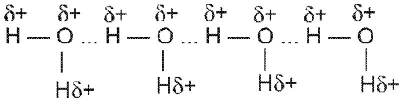
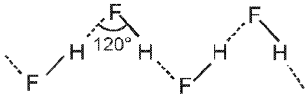
(B) Intermolecular H-Bonding :

it is formed between two different molecules of the same or different compounds.

(a) **In water molecules**



(b) The hydrogen bonds in HF link the F atom of one molecule with the H-atom of another molecule, thus forming a zig-zag chain $(HF)_n$ in both the solid and also in the liquid.



Intermolecular forces (Vander Waal's Forces) :

Intermolecular attractions hold two or more molecules together. These are weakest chemical forces and can be of following types.

(a) Ion-dipole attraction :

(b) Dipole-dipole attraction :

(c) Ion-induced dipole attraction :

(d) Dipole-induced dipole attraction :

(e) Instantaneous dipole- Instantaneous induced dipole attraction : (Dispersion force or London forces)

○ Strength of vander waal force ∝ molecular mass.

○ van der Waal's force ∝ boiling point.

Metallic bond :

Two models are considered to explain metallic bonding:

(A) Electron-sea model (B) Band model

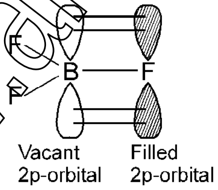
Some special bonding situations :

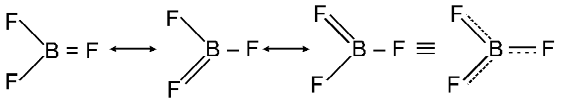
(a) Electron deficient bonding:

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds. These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) present in diborane B_2H_6, $Al_2(CH_3)_6$, $BeH_2(s)$ and bridging metal carbonyls.

(b) Back Bonding :

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals (generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length. For example, in BF_3





the extent of back bonding in boron trihalides.

$BF_3 > BCl_3 > BBr_3$

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COORDINATION COMPOUNDS

Addition Compounds :

They are formed by the combination of two or more stable compounds in stoichiometric ratio. These are

(1) Double salts and (2) Coordination compounds

Double salts :

Those addition compounds which lose their identity in solutions
eg. K_2SO_4 , $Al_2(SO_4)_3$

Coordination Compounds :

Those addition compounds which retain their identity (i.e. doesn't lose their identity) in solution are

$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2 . 4KCN$ or $K_4[Fe(CN)_6]$ (aq.) $\rightleftharpoons 4K^+$ (aq.) + $[Fe(CN)_6]^{4-}$ (aq.)

Central Atom/Ion :

In a coordination entity–the atom/ion to which are bound a fixed number of ligands in a definite geometrical arrangement around it.

Ligands :

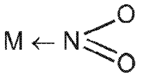
The neutral molecules, anions or cations which are directly linked with central metal atom or ion in the coordination entity are called ligands.

Chelate ligand :

Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring.

Ambidentate Ligand :

Ligands which can ligate through two different atoms present in it



$M \leftarrow N \overset{O}{\underset{O}{<}}$ nitrito-N ; $M \leftarrow O—N=O$ nitrito-O

$M \leftarrow SCN$ thiocyanato or thiocyanato-S ; $M \leftarrow NCS$ isothiocyanato or thiocyanato-N

Coordination Number :

The number of ligand donor atoms to which the metal is directly attached.

Oxidation number of Central Atom :

The oxidation number of the central atom is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. $[Fe(CN)_6]^{3-}$ is +3 and it is written as Fe(III).

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Denticity and Chelation :

Table : 1
Common Monodentate Ligands

Common Name	*IUPAC Name*	*Formula*
methyl isocyanide	methylisocyanide	CH_3NC
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh_3
pyridine	pyridine	C_5H_5N (py)
ammonia	ammine	NH_3
methyl amine	methylamine	$MeNH_2$
water	aqua or aquo	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO
fluoro	fluoro or fluorido*	F^-
chloro	chloro or chlorido*	Cl^-
bromo	bromo or bromido*	Br^-
iodo	iodo or iodido*	I^-
cyano	cyanido or cyanido-C* (C-bonded)	CN^-
isocyano	isocyanido or cyanido-N* (N-bonded)	NC^-
thiocyano	thiocyanato-S(S-bonded)	SCN^-
isothiocyano	thiocyanato-N(N-bonded)	NCS^-
cyanato (cyanate)	cyanato-O (O-bonded)	OCN^-
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO^-
hydroxo	hydroxo or hydroxido*	OH^-
nitro	nitrito–N (N–bonded)	NO_2^-
nitrito	nitrito–O (O–bonded)	ONO^-
nitrate	nitrato	NO_3^-
amido	amido	NH_2^-
imido	imido	NH^{2-}
nitride	nitrido	N^{3-}
azido	azido	N_3^-
hydride	hydrido	H^-
oxide	oxido	O^{2-}
peroxide	peroxido	O_2^{2-}
superoxide	superoxido	O_2^-
acetate	acetato	CH_3COO^-
sulphate	sulphato	SO_4^{2-}
thiosulphate	thiosulphato	$S_2O_3^{2-}$
sulphite	sulphito	SO_3^{2-}
hydrogen sulphite	hydrogensulphito	HSO_3^-
sulphide	sulphido or thio	S^{2-}
hydrogen sulphide	hydrogensulphido or mercapto	HS^-
thionitrito	thionitrito	$(NOS)^-$
nitrosylium	nitrosylium or nitrosonium	NO^+
nitronium	nitronium	NO_2^+

* The 2004 IUPAC draft recommends that anionic ligands will end with-ido.

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Table : 2

Common Chelating Amines

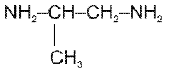
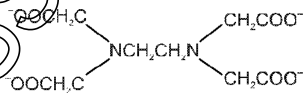
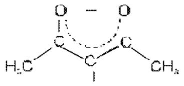
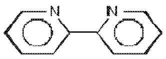
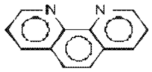
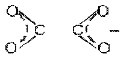
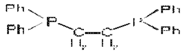
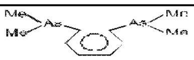
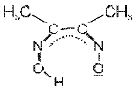
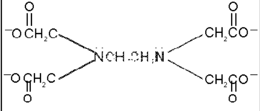
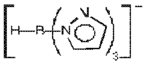
Chelating Points	Common Name	IUPAC Name	Abbreviation	Formula
bidentate	ethylenediamine	1,2-ethanediamine/ ethane-1,2-diamine	en	$NH_2,CH_2CH_2NH_2$
bidentate	propanediamine	1,2-propanediamine	pn	 $NH_2\text{–}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\text{–}CH_2\text{–}NH_2$
tridentate	diethylenetriamine	[N-(2-aminoethyl)-1 2-ethanediamine or diethylenetriamine	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
tetradenate	triethylenetetraamine	[N, N'-bis-(2-aminoethyl)-1, 2-ethanediamine or triethylenetetraamine	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	triaminotriethylamine	β,β′,β″-tris(2-aminoe- thyl) amine.	tren	 $NH_2CH_2CH_2\underset{\displaystyle CH_2CH_2NH_2}{\underset{\vert}{N}}CH_2CH_2NH_2$
pentadentate	tetraethylenepentaamine	1,4,7,10 pentaazatridecane or tetraethylenepentaamine		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
hexadentate	ethylenediaminetetraacetate	1,2–ethanediyl (dinitrilo) tetraacetate or ethylenediaminetetraacetate	EDTA	

Table : 3

Common Multidentate (Chelating) Ligands

Common Name	IUPAC Name	Abbreviation	Formula	Structure
acetylacetonato	2,4-pentanediono or acetylacetonato	acac	$CH_3COCHCOCH_3^-$	
2,2'-bipyridine	2,2'-bipyridyl	bipy	$C_{10}H_8N_2$	
1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen,o-phen	$C_{12}H_8N_2$	
oxalato	oxalato	ox	$C_2O_4^{2-}$	
dialkyldithiocarbamato	dialkylcarbamodithioato	dtc	$S_2CNR_2^-$	
1,2-bis(diphenylphophine)ethane	1,2-ethanediylbis (dipheylphosphene)	dppe	$Ph_2PC_2H_4PPh_2$	
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethylarsene)	diars	$C_6H_4(As(CH_3)_2)_2$	
dimethylglyoximato	butanedienedioxime or dimethylglyoximato	DMG	$HONC(CH_3)C(CH_3)NO^-$	
ethylenediaminetetraacetato	1,2-ethanediyl (dinitrilo)tetraacetato or ethylenediaminetetraacetato	EDTA	$(^-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$	
pyrazolylborato	hydrotris- (pyrazo-1-yl)borato			

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Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one type of donor groups, e.g., $[Cr(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one type of donor groups, e.g., $[Co(NH_3)_4Br_2]^+$, are known as heteroleptic.

Nomenclature of Coordination Compounds

Writing the formulas of Mononuclear Coordination Entities :

(i) The central atom is placed first.

(ii) The ligands are then placed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also placed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligands abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Writing the name of Mononuclear Coordination Compounds :

(i) Like simple salts the cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order (according to the name of ligand, not the prefix) before the name of the central atom/ion.

(iii) Names of the anionic ligands end in –o and those of neutral ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO, thiocarbonyl for CS and nitrosyl for NO. But names of cationic ligands end in–ium.

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the one kind of ligands in the coordination entity. When the names of the ligands include a numerical prefix or are complicated or whenever the use of normal prefixes creates some confusion, it is set off in parentheses and the second set of prefixes is used.

2	di	bis	**3**	tri	tris
4	tetra	tetrakis	**5**	penta	pentakis
6	hexa	hexakis	**7**	hepta	heptakis

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in the parentheses after the name of metal.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix - ate. For example, Co in a complex anion, $[Co(SCN)_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions.

iron (Fe)	ferrate	lead (Pb)	plumbate
silver (Ag)	argentate	tin (Sn)	stannate
gold (Au)	aurate		

(vii) The neutral complex molecule is named similar to that of the complex cation.

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Werner's Theory :

According to Werner most elements exhibit two types of valencies : (a) Primary valency and (b) Secondary valency.

(a) Primary valency :

This corresponds to oxidation state of the metal ion. This is also called principal, ionisable or ionic valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines.

(b) Secondary or auxiliary valency :

It is also termed as coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e. coordinate covalent bond type). In the modern terminology, such spatial arrangements are called coordination polyhedra and various possibilities are

C.N. = 2	linear	C.N. = 3	Triangular
C.N. = 4	tetrahedral or square planar	C.N. = 6	octahedral.

Effective Atomic Number Rule given by Sidgwick :

Effective Atomic Number (EAN) = Atomic no. of central metal – Oxidation state of central metal + No. of electrons donated by ligands.

Valence bond theory :

The model utilizes hybridisation of (n-1) d, ns, np or ns, np, nd orbitals of metal atom or ion to yield a set of equivalent orbitals of definite geometry to account for the observed structures such as octahedral, square planar and tetrahedral, and magnetic properties of complexes. The number of unpaired electrons, measured by the magnetic moment of the compounds determines which d-orbitals are used.

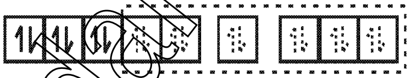
Table : 5

Coordiantion number of metal	Type of hybridisation	Shape of complex
4	sp^3	Tetrahedral
4	dsp^2	Square planer
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Coordination Number Six :

In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.

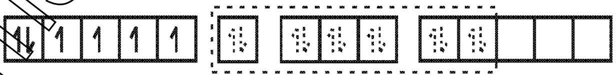
$[Co(NH_3)_6]^{3+}$



d^2sp^3 hybrid orbital

The complex $[FeF_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridisation (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So,

$[FeF_6]^{4-}$

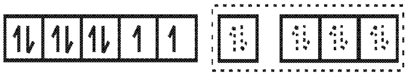


sp^3d^2 hybrid orbitals

Coordination Number Four :

In the paramagnetic and tetrahedral complex $[NiCl_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in figure.

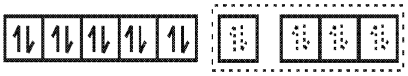
$[NiCl_4]^{2-}$



sp^3 hybrid orbitals

Similarly complex $[Ni(CO)_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridisation scheme is as shown in figure.

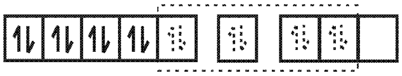
$[Ni(CO)_4]$



sp^3 hybrid orbitals

The hybridisation scheme for $[Ni(CN)_4]^{2-}$ is as shown in figure.

$[Ni(CN)_4]^{2-}$



dsp^2 hybrid orbitals

It suffers from the following shortcomings :

1. A number of assumptions are involved.
2. There is no quantitative interpretation of magnetic data.
3. It has nothing to say about the spectral (colour) properties of coordination compounds.
4. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
5. It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
6. It does not distinguish between strong and weak ligands.

Magnetic Properties of Coordination Compounds :

Magnetic Moment = $\sqrt{n(n+2)}$ Bohr Magneton ; n = number of unpaired electrons

For metal ions with upto three electrons in the d-orbitals like Ti^{3+}, (d^1) ; V^{3+} (d^2) ; Cr^{3+} (d^3) ; two vacant d-orbitals are easily available for octahedral hybridisation. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3d electrons are present, like in Cr^{2+} and Mn^{3+} (d^4) ; Mn^{2+} and Fe^{3+} (d^5) ; Fe^{2+} and Co^{3+} (d^6) ; the required two vacant orbitals for hybridisation is not directly available (as a consequence of Hund's rules). Thus, for d^4, d^5 and d^6 cases, two vacant d-orbitals are only available for hybridisation as a result of pairing of 3d electrons which leaves two, one and zero unpaired electrons respectively.

Crystal Field Theory :

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand.

(a) Crystal field splitting in octahedral coordination entities :

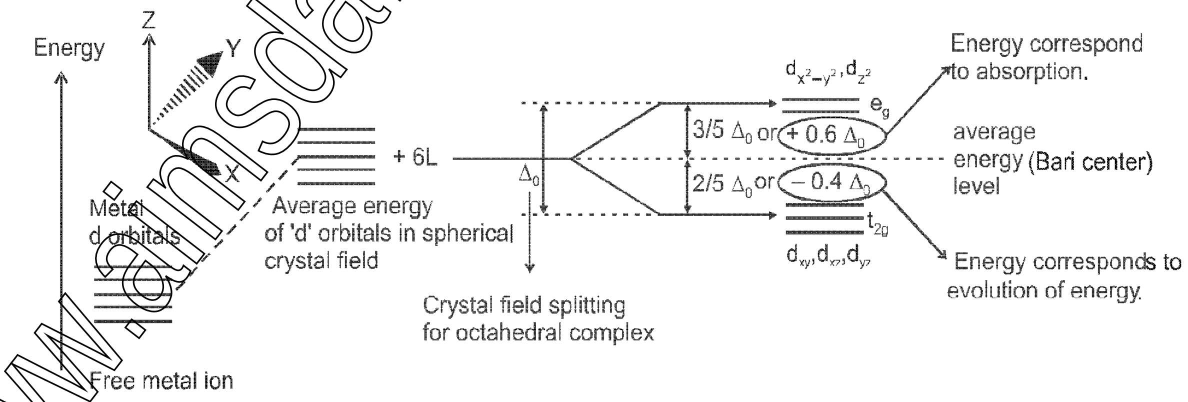


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0, depends upon the fields produced by the ligand and charge on the metal ion.

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Ligands can be arranged in a series in the orders of increasing field strength as given below :

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands.

Calculation of Crystal Field stabilisation energy (CFSE)

Formula : CFSE = $[-0.4 (n)\, t_{2g} + 0.6 (n')\, e_g]\, \Delta_0 + {}^*nP$.

where n & n′ are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. *n represents the number of extra electron pairs formed because of the ligands in comparison to normal degenerate configuration.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_0$.

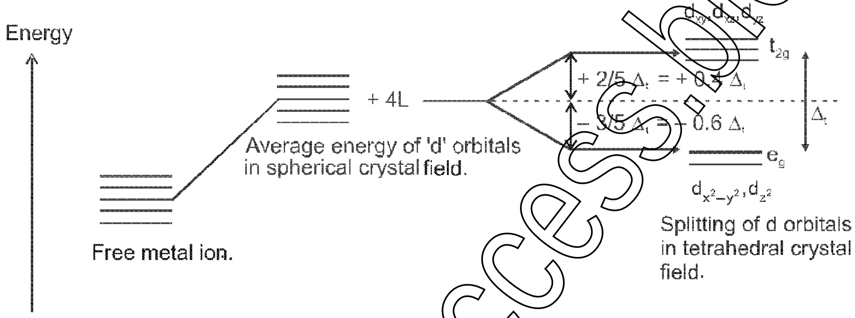


Figure showing crystal field splitting in tetrahedral complex.

COLOUR IN COORDINATION COMPOUNDS :

According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths.

Limitations of crystal field theory

(1) It considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals (such as s, p_x, p_y and p_z orbitals).

(2) It is unable to account satisfactorily for the relative strengths of ligands. For example it gives no explanation as to why H_2O is a stronger ligand than OH^- in the spectrochemical series.

(3) According to this theory, the bond between the metal and ligands are purely ionic. It gives no account on the partly covalent nature of the metal ligand bonds.

(4) The CFT cannot account for the π-bonding in complexes.

STABILITY OF COORDINATION COMPOUNDS :

The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$$

for the overall reaction :

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1, K_2, K_3, ... K_n for each step as represented below :

$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O$

$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$

$ML_{n-1}(H_2O) + L \rightleftharpoons ML_n + H_2O$

$K_n = [ML_n] / \{[ML_{n-1}(H_2O)] [L]\}$

$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$

$\beta_n = K_1 \times K_2 \times K_3 \times \ldots\ldots \times K_n$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium.

ISOMERISM :

(1) STRUCTURAL ISOMERISM :

(A) Ionisation isomerism :

This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand and can displace a ligand which can then become the counter ion.

$[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$

(B) Solvate / hydrate isomerism :

It occurs when water forms a part of the coordination entity or is outside it.

Complex	Reaction with $AgNO_3$	Reaction with conc. H_2SO_4(dehydrating agent)
$[Cr(H_2O)_6]Cl_3$	in the molar ratio of 3:1	No water molecule is lost or no reaction
$[CrCl(H_2O)_5]Cl_2.H_2O$	in the molar ratio of 2:1	one mole of water is lost per mole of complex
$[CrCl_2(H_2O)_4]Cl.2H_2O$	in the molar ratio of 1:1	two mole of water are lost per mole of complex

(C) Linkage isomerism :

In some ligands, like ambidentate ligands, there are two possible coordination sites. In such cases, linkage isomerism exist. e.g.,

For example : $[Co(ONO)(NH_3)_5]Cl_2$ & $[Co(NO_2)(NH_3)_5]Cl_2$.

(D) Coordination isomerism :

Coordination compounds made up of cationic and anionic coordination entities show this type of isomerism due to the interchange of ligands between the cation and anion entities. Some of the examples are :

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6](Co(CN)_6]$

(E) Ligand isomerism :

Since many ligands are organic compounds which have possibilities for isomerism, the resulting complexes can show isomerism from this source.

(F) Polymerisation isomerism :

Considered to be a special case of coordination isomerism, in this the various isomers differ in formula weight from one another, so not true isomers in real sense.

(2). Stereoisomerism

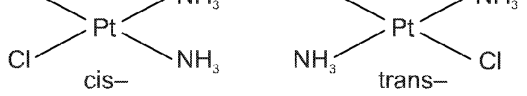
Geometrical Isomerism

Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

Coordination Number Four :

Tetrahedral Complex : The tetrahedral compounds can not show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.

Square Planar Complex :



cis– trans–

Geometrical isomers (cis and trans) of $Pt(NH_3)_2Cl_2$.

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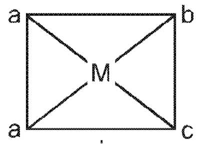
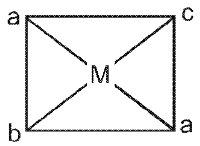
Square planar complex of the type Ma_2bc (where a,b,c are unidentates) shows two geometrical isomers.

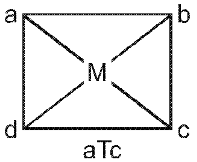


cis–

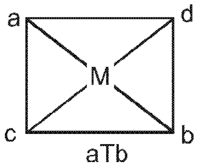


trans–

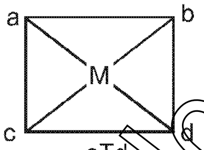
Square planar complex of the type Mabcd (where a,b,c,d are unidentates) shows three geometrical isomers.



aTc



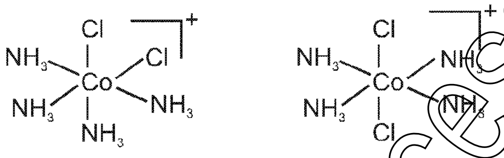
aTb



aTd

Coordination Number Six :

Geometrical isomerism is also possible in octahedral complexes.



cis– trans–

Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

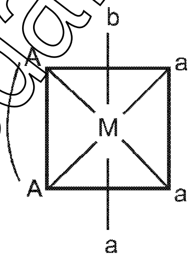
(I) Complexes containing only unidentate ligands

(i) **Ma_2b_4** – **2** ; (ii) **Ma_4bc** – **2**

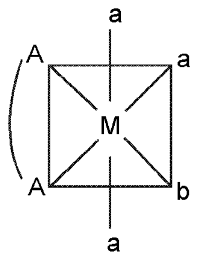
(iii) **Ma_3b_3**

(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)a_3b$ – Two geometrical isomers are possible.



bTa



aTa

(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.

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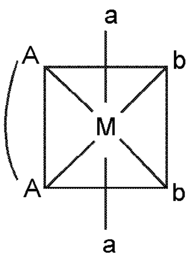
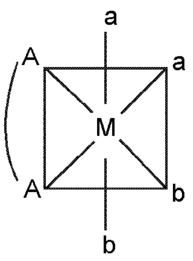
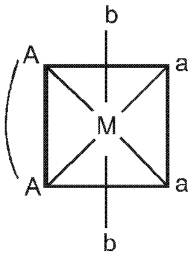


aTa



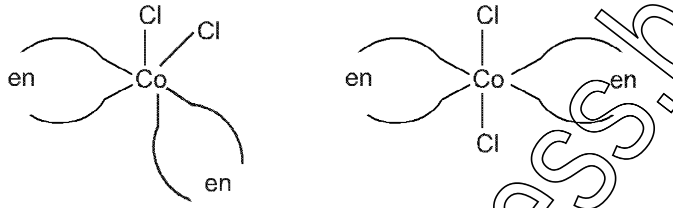
aTb



bTb

Note : With $[M(AA)b_4]$, only one form is possible. M(AA)abcd have six geometrical isomers.

(iii) $M(AA)_2O_2$ – Two geometrical isomers are possible.



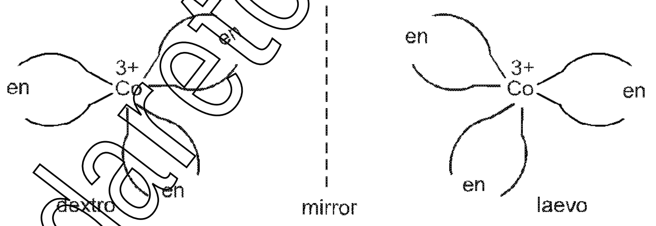
Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

Optical Isomerism :

A coordination compound which can rotate the plane of polarised light is said to be optically active.

Octahedral complex :

Optical isomerism is common in octahedral complexes involving didentate ligands. For example, $[Co(en)_3]^{3+}$ has d and ℓ forms as given below.



d and ℓ of $[Co(en)_3]^{3+}$

Square planar complex :

Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality.

Organometallic compounds

Metal Carbonyls :

Compounds of metals with CO as a ligand are called metal carbonyls.

They are of two types.

(a) **Monomeric :** Those metal carbonyls which contain only one metal atom per molecule are called monomeric carbonyls. For examples :$[Ni(CO)_4]$ (sp^3, tetrahedral) ; $[Fe(CO)_5]$ (dsp^3, trigonal bipyramidal).

(b) **Polymeric :** Those metal carbonyls which contain two or more than two metal atoms per molecule and they have metal-metal bonds are called polymeric carbonyl. For example : $Mn_2(CO)_{10}$, $Co_2(CO)_9$, etc.

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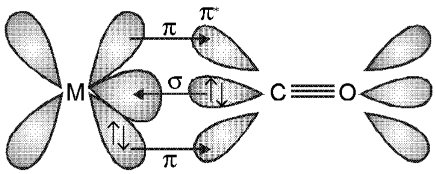
The M — C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. Thus carbon monoxide acts as σ donor (OC $\rightarrow$ M) and a π acceptor (OC $\leftarrow$ M), with the two interactions creating a synergic effect which strengthens the bond between CO and the metal as shown in figure.



Synergic bonding

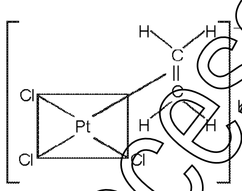
Sigma (σ) bonded organometallic compounds :

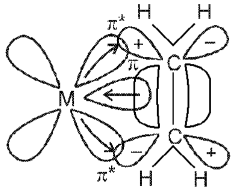
(a) Grignard's Reagent R – Mg – X where R is a alkyl or aryl group and X is halogen.
(b) $(CH_3)_4Sn$, $(C_2H_5)_4Pb$, $Al_2(CH_3)_6$, $Al_2(C_2H_5)_6$ etc.

Pie (π)-bonded organometallic compounds :

These are the compounds of metal with alkenes, alkynes, benzene and other ring compounds.

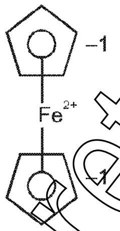
Zeise's salt : K [PtCl$_3$ (η^2 – C_2H_4)]



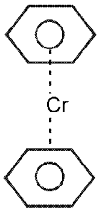


Ferrocene and bis(benzene)chromium **:**

Fe (η^5 – C_5H_5)$_2$



and Cr (η^6 – C_6H_6)$_2$



METALLURGY

The compound of a metal found in nature is called a mineral. The minerals from which metal can be economically and conveniently extracted are called **ores**. An ore is usually contaminated with earthy or undesired materials known as gangue.

(a) **Native ores** contain the metal in free state. Silver, gold, platinum etc, occur as native ores.
(b) **Oxidised ores** consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.
(c) **Sulphurised ores** consist of sulphides of metals like iron, lead, zinc, mercury etc.
(d) **Halide ores** consist of halides of metals.

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Metal	Ores	Composition
Aluminium	Bauxite	$AlO_X(OH)_{3-2X}$ [where $0 < X < 1$] Al_2O_3
	Diaspore	$Al_2O_3.H_2O$
	Corundam	Al_2O_3
	Kaolinite (a form of clay)	$[Al_2 (OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
	Limonite	$Fe_2O_3.3H_2O$
Copper	Copper pyrite	$CuFeS_2$
	Copper glance	Cu_2S
	Cuprite	Cu_2O
	Malachite	$CuCO_3.Cu(OH)_2$
	Azurite	$2CuCO_3.Cu(OH)_2$
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO
Lead	Galena	PbS
	Anglesite	$PbSO_4$
	Cerrusite	$PbCO_3$
Magnesium	Carnallite	$KCl.MgCl_2\ 6H_2O\ (K_2MgCl_4\ .6H_2O)$
	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3\ CaCO_3$
	Epsomsalt (Epsomite)	$MgSO_4\ 7H_2O$
	Langbeinite	$K_2Mg_2(SO_4)_3$
Tin	Cassiterite (Tin stone)	SnO_2
Silver	Silver glance (Argentite)	Ag_2S
	Chlorargyrite (Horn silver)	$AgCl$.

Metallurgy :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

(A) **Crushing and Grinding :** The ore is first crushed by jaw crushers and ground to a powder.

(B) **Concentration :**

The removal of unwanted useless impurities from the ore is called **dressing, concentration or benefaction of ore**.

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(i) Hydraulic washing or Gravity separation or Levigation method :
It is based on the difference in the densities of the gangue and ore particles. This method is generally used for the concentration of oxide and native ores.

(ii) Electromagnetic separation :
It is based on differences in magnetic properties of the ore components. Chromite ore($FeO.Cr_2O_3$) is separated from non–magnetic silicious impurities and cassiterite ore(SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$).

(iii) Froth floatation process. This method is commonly used for the concentration of the low grade sulphide ores like galena, PbS (ore of Pb) ; copper pyrites $Cu_2S.Fe_2S_3$ or $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc., and is based on the fact that gangue and ore particles have different degree of wettability with water and pine oil; the gangue particles are preferentially wetted by water while the ore particles are wetted by oil. In this process one or more chemical frothing agents are added.

(iv) Leaching : Leaching is often used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents.

(C) Extraction of crude metal from concentrated ore :
The isolation of metals from concentrated ore involves two major steps as given below.

(i) Conversion to oxide :

Calcination. It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes :
(a) The carbonate ore gets decomposed to form the oxide of the metal.
(b) Water of crystallisation present in the hydrated oxide ore gets lost as moisture.
(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

Roasting. It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. Roasting is an exothermic process once started it does not require additional heating.

Smelting :
Slag formation : In many extraction processes, an oxide is added deliberately to combine with other impurities and form a stable molten phase immiscible with molten metal called a slag. The process is termed smelting. The principle of slag formation is essentially the following :

Nonmetal oxide (acidic oxide) + Metal oxide (basic oxide) ⟶ Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in extraction of Cu from copper pyrite.

$$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$$

$$\underbrace{Cu_2S + FeO}_{\text{(roasted pyrite)}} + SiO_2 \longrightarrow \underset{\text{(upper layer)}}{FeSiO_3 \text{ (Fusible slag)}} + \underset{\text{(lower layer)}}{Cu_2S \text{ (matte)}}$$

Matte also contains a very small amount of iron(II) sulphide.
To remove unwanted acidic impurities like sand and P_4O_{10}, smelting is done in the presence of limestone.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (fusible slag)}$$

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2 \text{ (fusible slag - Thomas slag)}$$

(ii) Reduction of a metal oxide :
The free metal is obtained by reduction of a compound, using either a chemical reducing agent or electrolysis.

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Chemical reduction method :

Reduction with carbon :

$$PbO + C \longrightarrow Pb + CO \text{ (extraction of lead)}$$

Reduction with CO : In some cases CO produced in the furnace itself is used as a reducing agent.

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Reduction by other metals :

Metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to Al_2O_3. The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.

$$Cr_2O_3 + Al \rightarrow 2Cr\,(\ell) + Al_2O_3$$

Magnesium reduction method : Magnesium is used in similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.

$$TiCl_4 + 2\,Mg \xrightarrow[1000-1150°C]{\text{Kroll process}} Ti + 2\,MgCl_2$$

$$TiCl_4 + 4Na \xrightarrow{\text{IMI process}} Ti + 4\,NaCl$$

Self-reduction method :

This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate then that reacts with the remaining part of the sulphide ore to give its metal and SO_2.

$$Cu_2S + 3O_2 \longrightarrow 3Cu_2O + 2\,SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Electrolytic reduction :

It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals such as magnesium or aluminum or for production of samples of high purity.

1. **In aqueous solution :** Electrolysis can be carried out conveniently and cheaply in aqueous solution that the products do not react with water. Copper and zinc are obtained by electrolysis of aqueous solution of their sulphates.
2. **In fused melts :** Aluminum is obtained by electrolysis of a fused mixture of Al_2O_3 and cryolite $Na_3[AlF_6]$.

Extraction of Aluminium : It involves the following processes

(a) Purification of bauxite :

(i) Bayer's Method	**(ii) Hall's Method**	**(iii) Serpeck's Method**
(used for red bauxite containing Fe_2O_3 and silicates as impurities) $Al_2O_3 . 2H_2O + 2NaOH \xrightarrow[8\text{ atm}]{190°C}$ $2NaAlO_2$ (soluble) $+ 3H_2O$ Fe_2O_3 (insoluble) separated as red mud by filteration solution is diluted with water and seeded with freshly prepared $Al(OH)_3$. It induces the precipitation of $Al(OH)_3$. $Al(OH)_3$ is filtered leaving behind silicates in solution. $NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3\downarrow$ $2Al(OH)_3 \xrightarrow{1473K\ \Delta} Al_2O_3 + 3H_2O$	(used for red bauxite containing Fe_2O_3 and silicates as impurities) $Al_2O_3 . 2H_2O + Na_2CO_3 \xrightarrow{\text{Fuse}}$ $2NaAlO_2$ (soluble) $+ CO_2 + 2H_2O$ $2NaAlO_2 + 3H_2O + CO_2 \xrightarrow{60°C}$ $2Al(OH)_3\downarrow + Na_2CO_3$ $2Al(OH)_3 \xrightarrow{1473K\ \Delta} Al_2O_3 + 3H_2O$	(used for white bauxite containing silica as impurities) $Al_2O_3 . 2H_2O + 3C + N_2 \xrightarrow[\text{Electric furnace}]{1800°C}$ $2AlN + 3CO + 2H_2O$ $2AlN + 3H_2O \rightarrow Al(OH)_3\downarrow + NH_3$ $SiO_2 + 2CO \rightarrow 2CO_2 + Si$ Silicone volatilises at this temp. $2Al(OH)_3 \xrightarrow{1473K\ \Delta} Al_2O_3 + 3H_2O$

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(b) Electrolytic reduction (Hall-Heroult process) :

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

Cathode : Al^{3+} (melt) + $3e^- \longrightarrow Al(l)$

Anode : $C(s) + O^{2-}$ (melt) $\longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}$ (melt) $\longrightarrow CO_2(g) + 4e^-$

Metallurgy of some important metals

1. Extraction of iron from ore haematite :

Reactions involved :

At 500 – 800 K (lower temperature range in the blast furnace)

$$3\,Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3Fe + 4\,CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \longrightarrow 2\,CO\ ; \qquad FeO + CO \longrightarrow Fe + CO_2$$

Limestone is also decomposed tom CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

$$CaCO_3 \longrightarrow CaO + CO_2\ ; \qquad CaO + SiO_2 \longrightarrow CaSiO_3$$

2. Extraction of copper :

From copper glance / copper pyrite (self reduction) :

$$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$$

$Cu_2S + FeO + SiO_2 \longrightarrow FeSiO_3$ (fusible slag) + Cu_2S (matte)

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\ ; \qquad FeO + SiO_2 \longrightarrow FeSiO_3$$

$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$; $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (self reduction)

3. Extraction of lead :

(i) $$2PbS(s) + 3O_2(g) \xrightarrow{\Delta} 2PbO(s) \xrightarrow[\Delta]{+C} 2Pb(\ell) + CO_2(g)$$

(ii) $$3PbS(s) \xrightarrow[\text{air}]{\text{heat in}} PbS(s) + 2PbO(s) \xrightarrow[\text{absence of air}]{\text{Heat in}} 3Pb(\ell) + SO_2(g)$$

4. Extraction of zinc from zinc blende :

The ore is roasted in presence of excess of air at temperature 1200 K.

$$2\,ZnS + 3O_2 \longrightarrow 2\,ZnO + 2SO_2$$

The reduction of zinc oxide is done using coke.

$$ZnO + C \xrightarrow{\text{Coke, 1673 K}} Zn + CO$$

5. Extraction of tin from cassiterite :

The concentrated ore is subjected to the electromagnetic separation to remove magnetic impurity of Wolframite. SnO_2 is reduced to metal using carbon at 1200 – 1300°C in an electric furnace. The product often contains traces of Fe, which is removed by blowing air through the molten mixture to oxidise FeO which then floats to the surface.

$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

$$2Fe + O_2 \longrightarrow 2FeO$$

6. Extraction of Magnesium :

From Sea water (Dow's process) :

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) Precipitation of magnesium as magnesium hydroxide by slaked lime.

(b) Preparation of hexahydrated magnesium chloride.

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The solution on concentration and crystallisation gives the crystals of $MgCl_2.6H_2O$.

(c) Preparation of anhydrous magnesium chloride.

(d) Electrolysis of fused anhydrous $MgCl_2$ in presence of NaCl.

$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

At cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$(99% pure) ; **At anode :** $2Cl^- \longrightarrow Cl_2 + 2e^-$

7. Extraction of gold and silver (MacArthur-Forrest cyanide process) :

(a) From native ores : Extraction of gold and silver involves leaching the metal with CN^-.

$$4Au / Ag\ (s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[Au / Ag\ (CN)_2]^-(aq) + 4OH^-(aq)$$

$$2[Au / Ag\ (CN)_2]^-(aq) + Zn(s) \longrightarrow 2Au / Ag\ (s) + [Zn(CN)_4]^{2-}\ (aq)$$

(b) From argentite ore :

$$Ag_2S \text{ (conc. ore)} + 2NaCN \xrightleftharpoons{Air} 2AgCN + Na_2S.$$

$$4Na_2S + 5O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

$$AgCN + NaCN \longrightarrow Na[Ag(CN)_2] \text{ (soluble complex)}$$

$$2Na[Ag(CN)_2] + Zn \text{ (dust)} \longrightarrow 2Ag\downarrow + Na_2[Zn(CN)_4].$$

(D) Purification or Refining of metals :

Physical methods : These methods include the following processes :

(I) Liquation process : This process is used for the purification of the metal, which itself is readily fusible, but the impurities present in it are not, used for the purification of Sn and Zn, and for removing Pb from Zn-Ag alloy.

(II) Fractional distillation process : This process is used to purify those metals which themselves are volatile and the impurities in them are nonvolatile and vice-versa. Zn, Cd and Hg are purified by this process.

(III) Zone refining method (Fractional crystallisation method) : This process is used when metals are required in very high purity, for specific application. For example pure Si and Ge are used in semiconductors

Chemical methods : These methods include the following methods :

(I) OXIDATIVE REFINING :

This method is usually employed for refining metals like Pb, Ag, Cu, Fe, etc. In this method the molten impure metal is subjected to oxidation by various ways.

(II) POLING PROCESS :

This process is used for the purification of copper and tin which contains the impurities of their own oxides.

$$\text{Green wood} \rightarrow \text{Hydrocarbons} \rightarrow CH_4$$

$$4CuO + CH_4 \rightarrow 4Cu \text{ (pure metal)} + CO_2 + 2H_2O$$

(III) ELECTROLYTIC REFINING :

Some metals such as Cu, Ni, and Al are refined electrolytically.

(IV) VAPOR PHASE REFINING :

(i) Extraction of Nickel (Mond's process) : The sequence of reaction is

$$H_2O(g) + C \longrightarrow CO(g) + H_2$$

$$Ni(s) + 4\ CO(s) \xrightarrow{50°C} [Ni(CO_4)]\ (g)$$

$$[Ni\ (CO)_4](g) \xrightarrow{200°C} Ni + 4CO(g)$$

(ii) Van Arkel–De Boer process :

$$\text{Impure Ti} + 2I_2 \xrightarrow{50-250°C} TiI_4 \xrightarrow[\text{Tungsten filament}]{1400°C} Ti + 2I_2$$

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s-BLOCK ELEMENTS & THEIR COMPOUNDS

Group 1 of the periodic table consists of the elements : lithium, sodium, potassium, rubidium, caesium and francium .

The elements of Group 2 include beryllium, magnesium, calcium, strontium, barium and radium.

Hydration Enthalpy :

The hydration enthalpies of alkali metal ions decrease with increase in ionic sizes. Li^+ has maximum degree of hydration and for this reasons lithium salts are mostly hydrated e.g., $LiCl \cdot 2H_2O$

Physical properties :

All the alkali metal are silvery white, soft and light metals. Because of the larger size, these element have low density. The melting and boiling point of the alkali metals are low indicating weak metallic bonding alkali metals and their salts impart characteristic colour to an oxidizing flame.

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet/ Lilac	Red violet	Blue

Chemical Properties:

The alkali metal are highly reactive due to their larger size and low ionization enthalpy.

- **Reactivity towards air :** They burn vigorously in oxygen forming oxides. Lithium forms monoxide, sodium forms peroxide, the other metals form superoxide.
- **Reducing nature:** The alkali metals, are strong reducing agents, lithium being the most and sodium the least powerful.
- **Solution in liquid ammonia:** The alkali metals dissolve in liquid ammonia giving deep blue solution which are conducting in nature.

$$M + (x + y)\,NH_3 \longrightarrow [M(NH_3)_x]^+ + [e(NH_3)_y]^-$$

The blue colour of the solution is due to the ammoniated electron and the solutions is paramagnetic.

$$M^+(am) + e^- + NH_3(\ell) \xrightarrow{\text{on standing}} MNH_2(am) + 1/2\,H_2(g)$$

In concentrated solution, the blue colour changes to bronze colour and becomes, diamagnetic.

ANOMALOUS PROPERTIES OF LITHIUM

(i) exceptionally small size of its atom and ion, and (ii) high polarising power (i.e., charge/ radius ratio).

The similarity between lithium and magnesium is particularly striking and arises because of their similar size: atomic radii, Li = 152 pm, Mg = 160 pm; ionic radii : Li^+ = 76 pm, Mg^{2+} = 72 pm.

GROUP 2 ELEMENTS : ALKALINE EARTH METALS

The first element beryllium differs from the rest of the member and shows diagonal relationship to aluminium.

Hydration Enthalpies

Hydration enthalpies of alkaline earth metal ions. $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. The hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Thus, compounds of alkaline earth metals are more extensively hydrated than those of alkali metals , e.g., $MgCl_2$ and $CaCl_2$ exist as $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ while NaCl and KCl do not form such hydrates.

Physical Properties

The alkaline earth metals, in general, are silvery white, lustrous and relatively soft but harder than the alkali metals. The melting and boiling point of these metals are higher due to smaller sizes. Because of the low ionisation enthalpies they are strongly electropositive in nature. The electrons in beryllium and magnesium are too strongly bound to get excited by flame. Hence these elements do not impart any colour to the flame. Calcium, strontium and barium impart characteristic colour to the flame.

Metal	Be	Mg	Ca	Sr	Ba
Colour	No colour	No colour	Brick red	Crimson	Apple green

Chemical Properties

❍ **Reactivity towards air and water :** Beryllium and magnesium are inert to oxygen and water. Magnesium is more electropositive and burns with dazzling brilliance in air to give MgO and Mg_3N_2 . Calcium, strontium and barium are readily attacked by air to form the oxide and nitride.

❍ **Reducing nature :** The alkaline earth metals are strong reducing agent. This is indicated by large negative value of their reduction potentials.

❍ **Solution in liquid ammonia:** The alkaline earth metals dissolve in liquid ammonia to give deep blue black solution forming ammoniated ions.

$$M + (x + y)\ NH_3 \rightarrow [\ M(NH_3)_x]^{2+} + 2\ [e(NH_3)_Y\ ]^-$$

From these solutions, the ammoniates, $[M(NH_3)_6]^{2+}$ can be recovered.

ANOMALOUS BEHAVIOUR OF BERYLLIUM

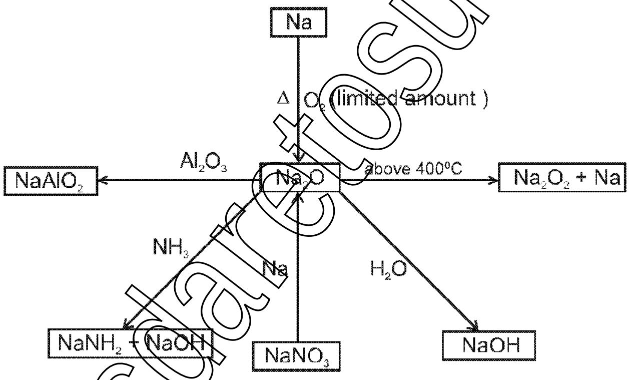
Beryllium the first member of the Group 2 metals, shows anomalous behaviour as compared to magnesium and rest of the members. Further, it shows diagonal relationship to aluminium.

Diagonal Relationship between Beryllium and Aluminium

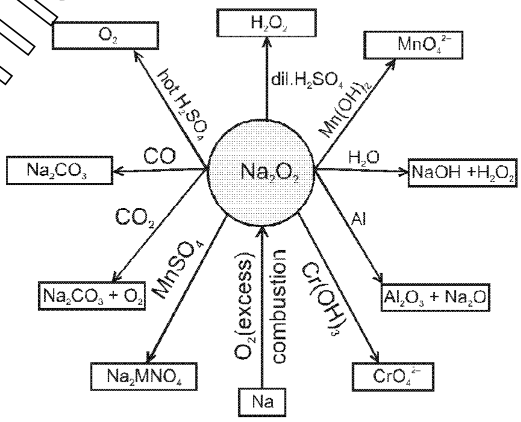
The ionic radius of Be^{2+} is estimated to be 31 pm; the charge/radius ratio is nearly the same as that of the Al^{3+} ion. Hence beryllium resembles aluminium in some ways.

Compounds of s-block elements :

1. **Sodium Oxide (Na_2O) :**



2. **Sodium peroxide (Na_2O_2) :**



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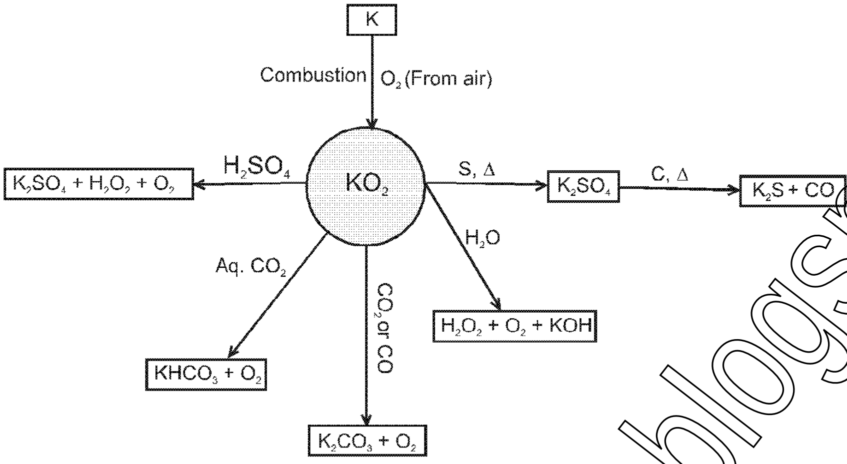
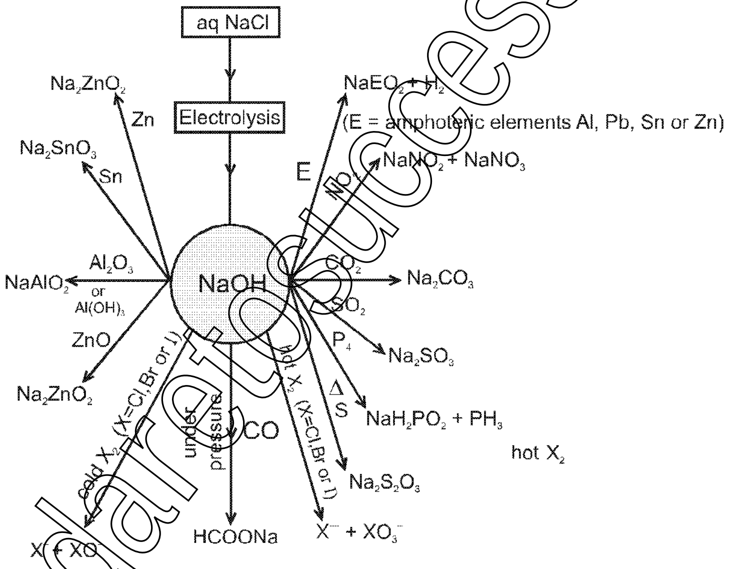
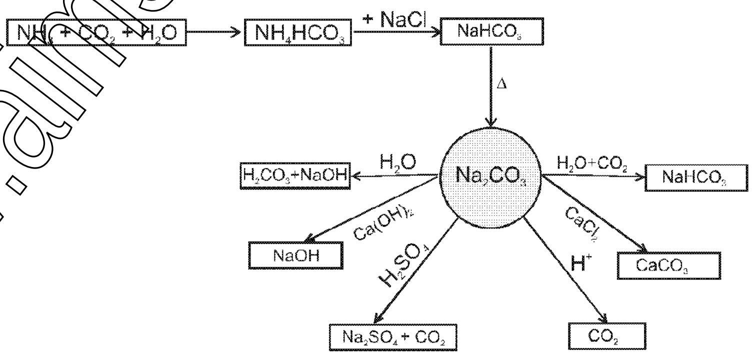
3. Potassium Super oxide (KO_2) :



4. Sodium Hydroxide (NaOH) :



5. Sodium Carbonate (Na_2CO_3) :



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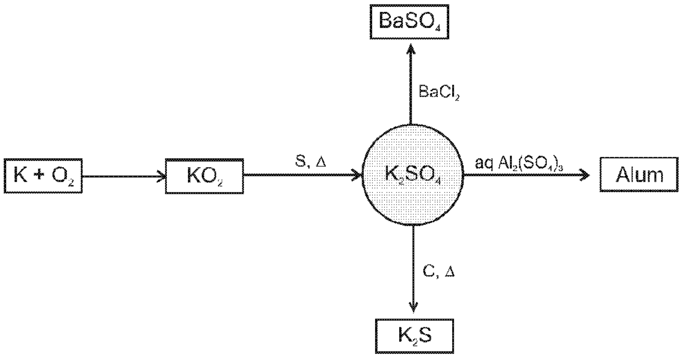
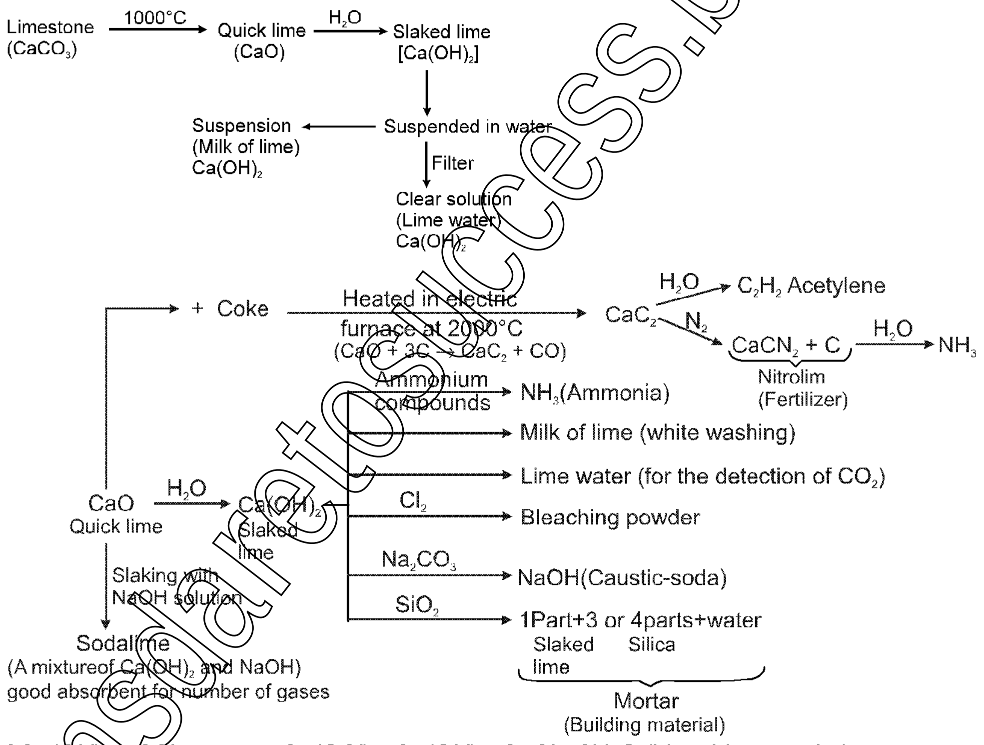
6. Potassium sulphate (K_2SO_4) :



7. Quick Lime, Slaked Lime and Lime Water :



$$3Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 . Ca(OH)_2 . CaCl_2 . 2H_2O \text{ (bleaching powder).}$$

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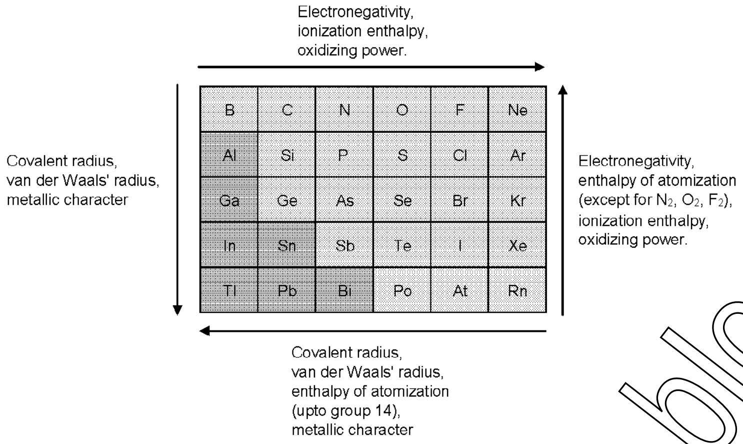
p-BLOCK ELEMENTS & THEIR COMPOUNDS

TRENDS IN PROPERTIES OF p-BLOCK ELEMENTS.



B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn

(A) GROUP 13 ELEMENTS : THE BORON FAMILY

Oxidation state and trends in chemical reactivity :

General Oxidation State = + 3.

Reactivity towards acids and alkalies

$$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 6\,Cl^{-}(aq) + 3\,H_2(g)$$

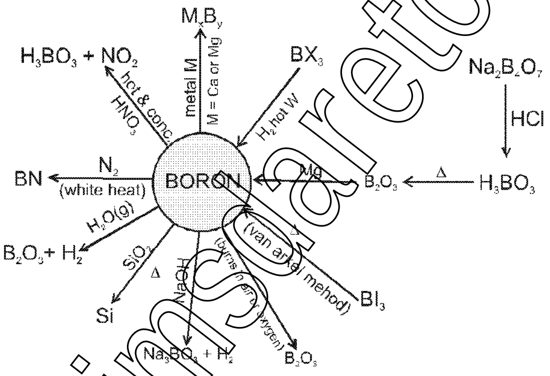
$$2Al(s) + 2NaOH\,(aq) + 6H_2O\,(1) \longrightarrow \underset{\text{Sodium tetrahydroxoaluminate (III)}}{2Na^{+}\,[Al(OH)_4]^{-}\,(aq)} + 3H_2(g)$$

Reactivity towards halogens

$$2E(s) + 3X_2\,(g) \rightarrow 2EX_3\,(s) \qquad (X = F, Cl, Br, I)$$

BORON (B):

Some Important Reactions of Boron and its compounds :



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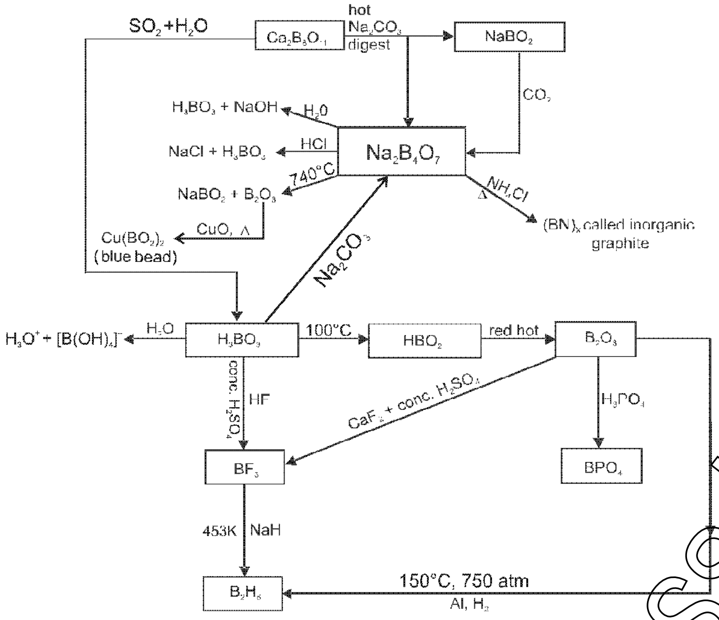

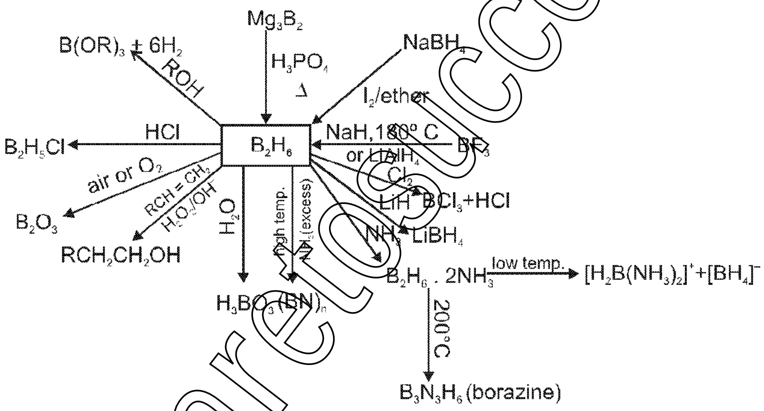

- Small amines such as NH_3, CH_3NH_2 and $(CH_3)_2NH$ give unsymmetrical cleavage of diborane.
  $B_2H_6 + 2NH_3 \longrightarrow [H_2B\ (NH_3)_2]^+ + [BH_4]^-$
- Large amines such as $(CH_3)_3N$ and pyridine give symmetrical cleavage of diborane.
  $2(CH_3)_3N + B_2H_6 \longrightarrow 2H_3B \longleftarrow N(CH_3)_3$
- $B_2H_6 + 2CO \xrightarrow{200°C,\ 20\ atm} 2BH_3CO$ (borane carbonyl)

(B) GROUP 14 ELEMENTS : THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14.

Electronic Configuration = $ns^2 np^2$.

Oxidation states and trends in chemical reactivity

Common oxidation states = +4 and +2. Carbon also exhibits negative oxidation states. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb.

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(i) Reactivity towards oxygen :
All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula MO and MO_2 respectively.

(ii) Reactivity towards water :
Tin decomposes steam to form dioxide and dihydrogen gas.

(iii) Reactivity towards halogen :
These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl Br, I). Stability of dihalides increases down the group.

ANOMALOUS BEHAVIOUR OF CARBON :

Catenation :

The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation. Due to the property of catenation and $p\pi$-$p\pi$ bonds formation, carbon is able to show allotropic forms.

Bond	Bond enthalpy (kJ mol^{-1})	Bond	Bond enthalpy (kJ mol^{-1})
C—C	**348**	**Si—Si**	**297**
Ge—Ge	**260**	**Sn—Sn**	**240**

Allotropes of Carbon

Diamond :

Crystalline lattice sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral manner. The C–C bond length is 154 pm. and produces a rigid three dimensional network of carbon atoms.

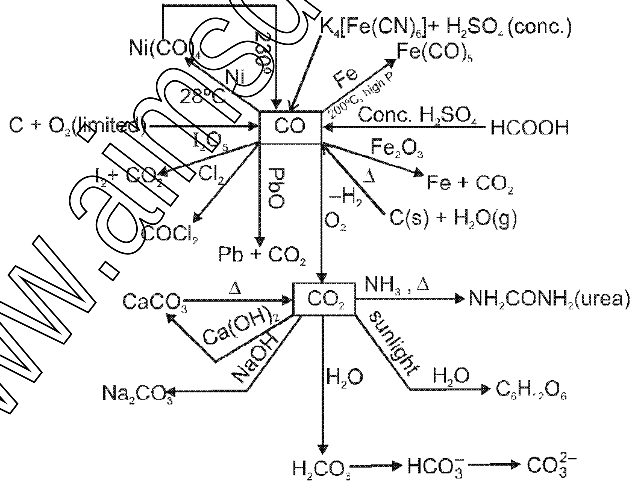
Graphite :

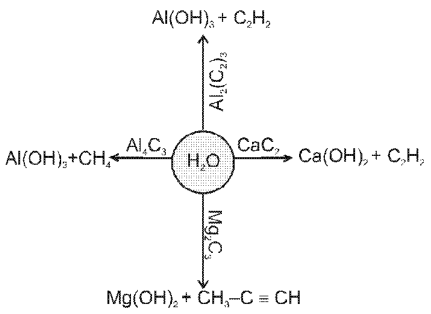
Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm. Each carbon atom in hexagonal ring undergoes sp^2 hybridisation graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature.

Fullerenes :

C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene.** It contains twenty six -membered rings and twelve five membered rings. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively.

SOME IMPORTANT REACTIONS OF CO, CO_2 AND METAL CARBIDES :





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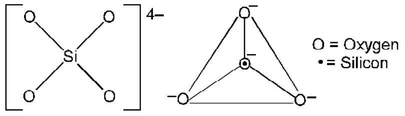
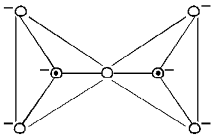
CLASSIFICATION OF SILICATES :

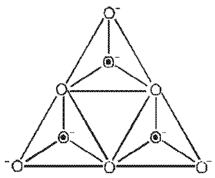
(A) Orthosilicates :



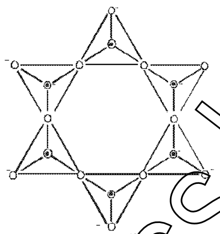
(B) Pyrosilicate :



(C) Cyclic silicates :

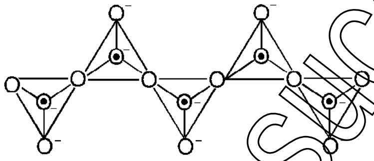


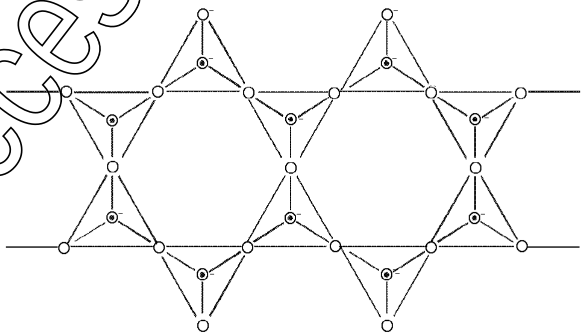
$Si_3O_9^{6-}$



$Si_6O_{18}^{12-}$

(D) Chain silicates :





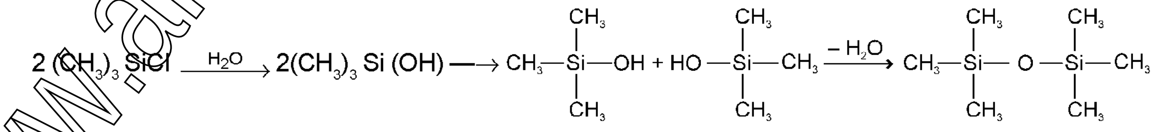
(E) Two dimensional sheet silicates :
In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$

(F) Three dimenstional sheet silicates :
These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

SILICONES :

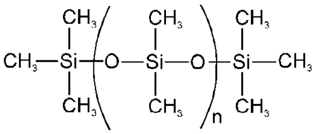
☞ Silicones can be prepared from the following types of compounds only.
(i) R_3SiCl (ii) R_2SiCl_2 (iii) $RSiCl_3$

☞ Silicones from the hydrolysis of $(CH_3)_3$ SiCl



$$2(CH_3)_3SiCl \xrightarrow{H_2O} 2(CH_3)_3Si(OH) \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-OH + HO-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 \xrightarrow{-H_2O} CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

☞ Silicones from the hydrolysis of a mixture of $(CH_3)_3$ SiCl & $(CH_3)_2$ $SiCl_2$



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-\left(O-\underset{CH_3}{\overset{CH_3}{Si}}-O\right)_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

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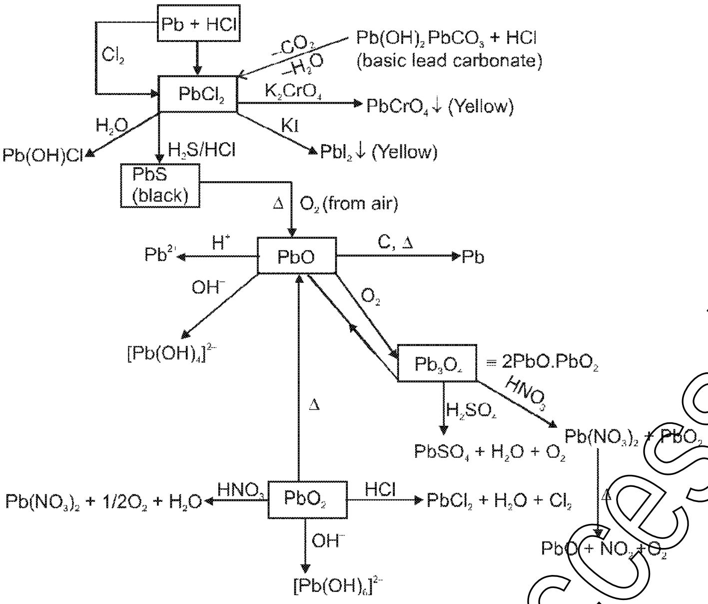
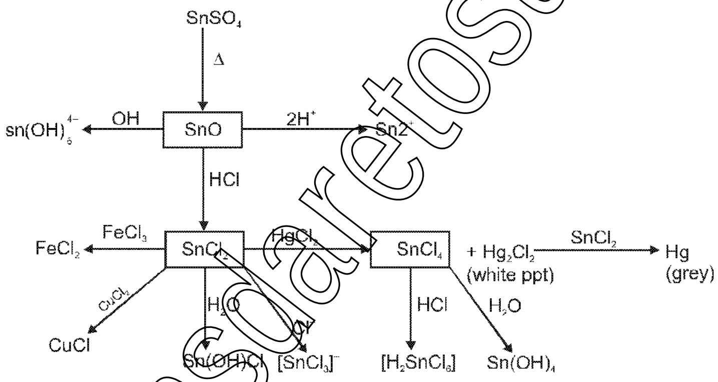
- When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained.
- The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

COMPOUNDS OF LEAD :



COMPOUNDS OF TIN :



(C) **GROUP 15 ELEMENTS : *THE NITROGEN FAMILY***

Electronic Configuration : $ns^2\ np^3$.

Atomic and Ionic Radii : Covalent and ionic (in a particular state) radii increase in size down the group.

Physical Properties:

All the elements of this group are polyatomic. Metallic character increases down the group. The boiling points , in general , increase from top to bottom in the group but the melting point increases upto arsenic and then decreases upto bismuth. Except nitrogen , all the elements show allotropy.

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Chemical Properties :

Oxidation States and trends in a chemical reactivity :

The common oxidation states of these elements are –3, +3 and +5. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group ; $Bi^{3+} > Sb^{3+} > As^{3+}$; $Bi^{5+} < Sb^{5+} < As^{5+}$ Nitrogen exhibits +1, +2, +4 oxidation states also when it reacts with oxygen.

Anomalous properties of nitrogen :

(i) The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. Consequently , the reducing character of the hydrides increases. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 \geq BiH_3$.

PROPERTIES OF HYDRIDES OF GROUP 15 ELEMENTS

Property	**NH_3**	**PH_3**	**AsH_3**	**SbH_3**	**BiH_3**
Melting point / K	195.2	139.5	156.7	185	–
Boiling point / K	238.5	185.5	210.6	254.6	290
(E – H) Distance / pm	101.7	141.9	151.9	170.7	–
HEH angle (^{0})	107.8	93.6	91.8	91.3	–
$\Delta_f H^- / kJ\ mol^{-1}$	– 46.1	13.4	66.4	145.1	278
$\Delta_{diss} H^-(E - H) / kJ\ mol^{-1}$	389	322	297	255	–

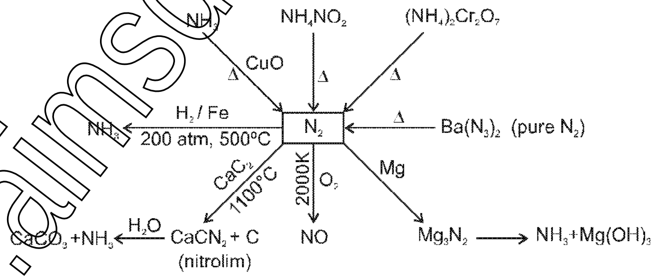
(ii) The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

(iii) Nitrogen does not form pentahalide due to non – availability of the d-orbitals in its valence shell. Pentahalides are more covalent than trihalides. Halides are hydrolysed in water forming oxyacids or oxychlorides.

$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$;
$SbCl_3 + H_2O \longrightarrow SbOCl \downarrow$ (orange) + 2HCl ;
$BiCl_3 + H_2O \longrightarrow BiOCl \downarrow$ (white) + 2HCl

(iv) These elements react with metals to form their binary compounds exhibiting –3 oxidation state , such as, Ca_3N_2 (calcium nitride) Ca_3P_2 (calcium phosphide) and Na_3As_2 (sodium arsenide).

NITROGEN (N) AND ITS COMPOUNDS :



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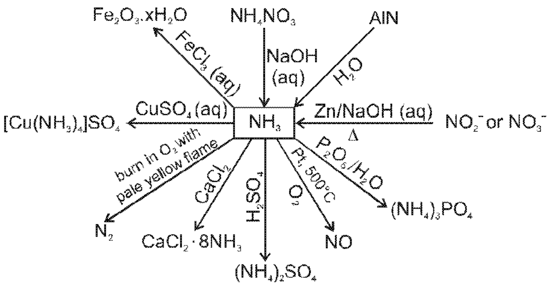
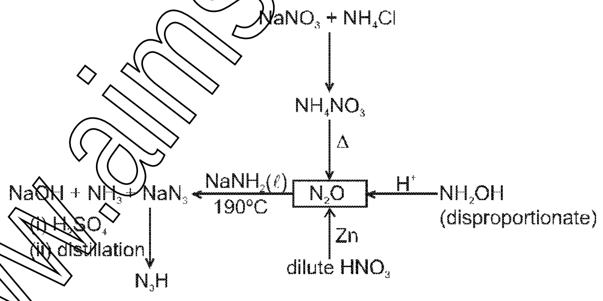
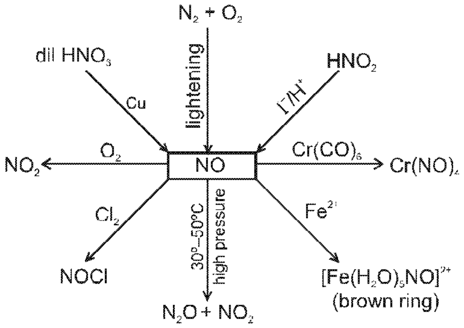


$CaO + H_2O \rightarrow Ca(OH)_2$; used for drying of NH_3

Oxides of Nitrogen

Name	Formula	Oxidation state of nitrogen	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N_2O	+ 1	$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	colourless gas , neutral
Nitrogen monoxide [Nitrogen(II) oxide] (Nitric acid)	NO	+ 2	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$	colourless gas , neutral
Dinitrogen trioxide [Nitrogen(III) oxide] (Nitrogen sesquioxide)	N_2O_3	+ 3	$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$	blue solid , acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO_2	+ 4	$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$	brown gas, acidic
Dinitrogen tetraoxide [Nitrogen(IV) oxide]	N_2O_4	+ 4	$2NO_2 \underset{Heat}{\overset{cool}{\rightleftharpoons}} N_2O_4$	colourless solid / liquid , acidic
Dinitrogen pentoxide [Nitrogen(IV) oxide]	N_2O_5	+ 5	$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$	colourless solid, acidic





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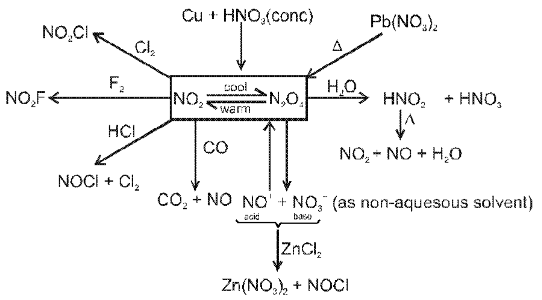
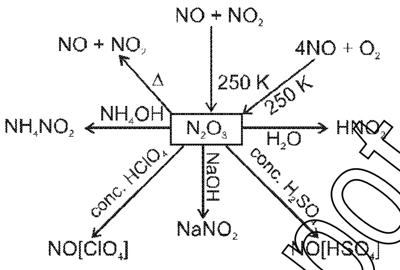
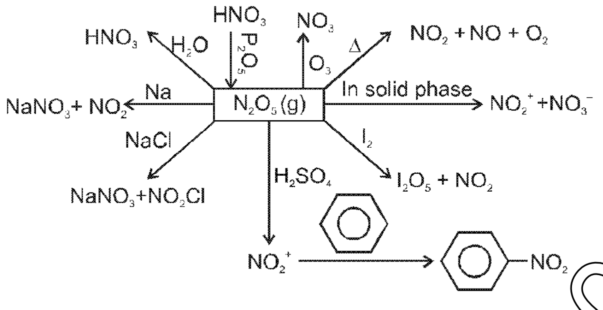
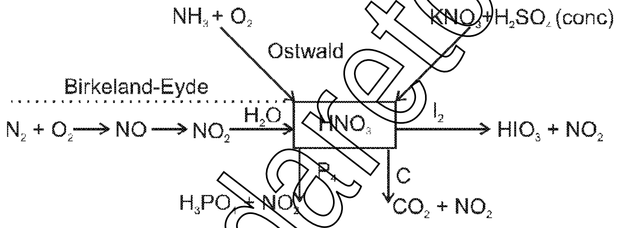




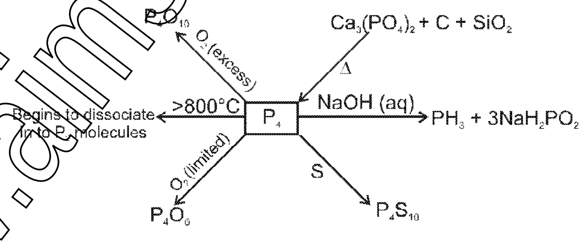


Sn	(a) dilute	NH_4NO_3	$4Sn+10HNO_3 \rightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$
	(b) concentrated	NO_2	$Sn + 4HNO_3 \rightarrow \underset{\text{meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$

antimonic acid



PHOSPHORUS (P) AND ITS COMPOUNDS :



When white phosphorus is heated in the atmosphere of CO_2 or coal gas at 573 K red phosphorus is produced. α-black phosphorus is formed when red phosphorus is heated in a sealed tube at 803 K. β-black phosphorus is prepared by heating white phosphorus at 473 K under high pressure.

Order of thermodynamic stability of various allotropes of phosphorus : black > red > white

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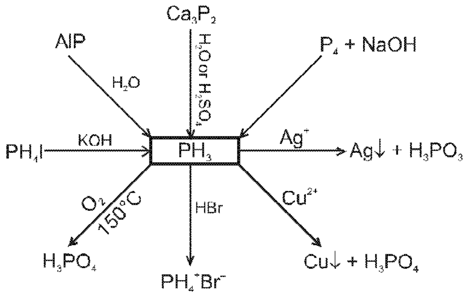
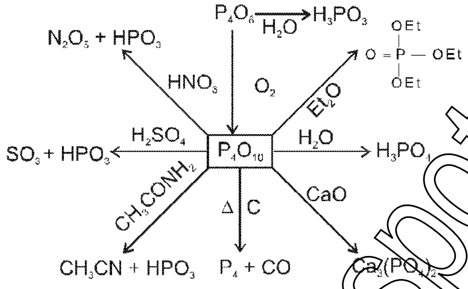
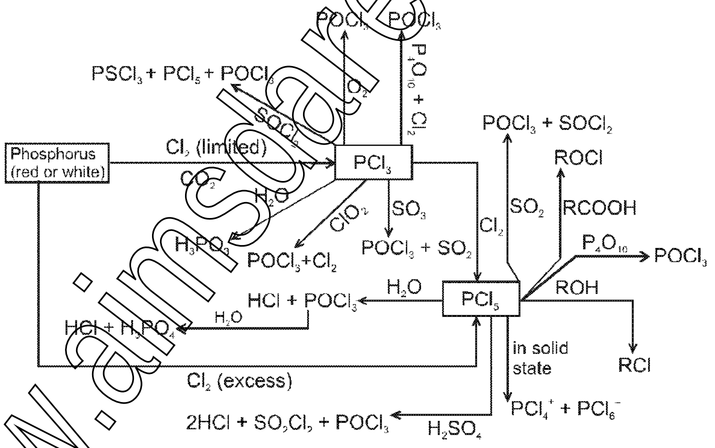




Oxoacids of Phosphorus

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous	H_3PO_2	+ 1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous	H_3PO_3	+ 3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+ 3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+ 5	Three P – OH One P = O	$P_4O_{10} + H_2O$
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric	$(HPO_3)_3$	+ 5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2 , heat in sealed tube



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(D) GROUP 16 ELEMENTS : THE OXYGEN FAMILY

Electronic Configuration : $ns^2\ np^4$.

Atomic and Ionic Radii :
Due to increase in the number of shells , atomic and ionic radii increase from top to bottom in the group. The size of oxygen atoms is however, exceptionally small.

Physical Properties :
Oxygen and sulphur are non-metal, selenium and tellurium metalloids, whereas polonium is a metal. Polonium is radioactive and is short lived (Half-life 13.8 days). The melting and boiling points increase with an increase in atomic number down the group.

Catenation :
Tendency for catenation decreases down the group. This property is prominently displayed by sulphur (S_8). The S—S bond is important in biological system and is found in some proteins and enzymes such as cysteine.

Chemical Properties

Oxidation states and trends in chemical reactivity :
Elements of the group exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.

Anomalous behaviour of oxygen :

The anomalous behaviour of oxygen is due to its small size and high electronegativity. The absence of d orbitals in oxygen limits its covalency to four.

(i) Their acidic character increases from H_2O to H_2Te. The increase in acidic character can be understood in terms of decrease in bond (H-E) dissociation enthalpy down the group. Owing to the decrease in bond (H-E) dissociation enthalpy down the group , the thermal stability of hydrides also decreases from H_2O to H_2Po. All the hydrides except water possess reducing property and this property increases from H_2S to H_2Te.

PROPERTIES OF HYDRIDES OF GROUP 16 ELEMENTS

Property	H_2O	H_2S	H_2Se	H_2Te
m.p./K	273	188	208	222
b.p./K	373	213	232	269
H-E distance/pm	96	134	146	169
HEH angle (°)	104	92	91	90
$\Delta_f H$/kJ mol^{-1}	-286	-20	73	100
$\Delta_{diss} H$ (H-E)/kJ mol^{-1}	463	347	276	238
Dissociation constant[a]	1.8×10^{-16}	1.3×10^{-7}	1.3×10^{-4}	2.3×10^{-3}

(ii) Reducing property of dioxide decreases from SO_2 to TeO_2 ; SO_2 is reducing while TeO_2 is an oxidising agent. Oxides are generally acidic in nature.

(iii) The stabilities of the halides decrease in the order F > Cl > Br > I. Sulphur hexafluoride SF_6 is exceptionally stable for steric reasons.
The well known monohalides are dimeric in nature, Examples are S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2 and Se_2Br_2. These dimeric halides undergo disproportionation as given below :

$$2Se_2Cl_2 \longrightarrow SeCl_4 + 3Se.$$

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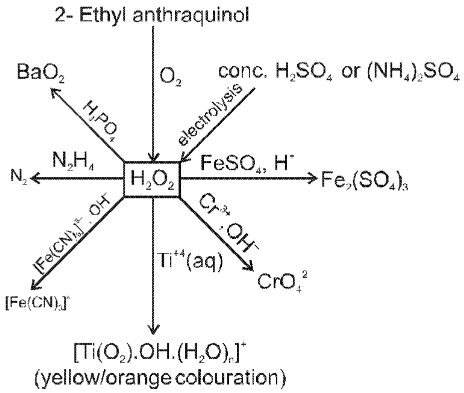
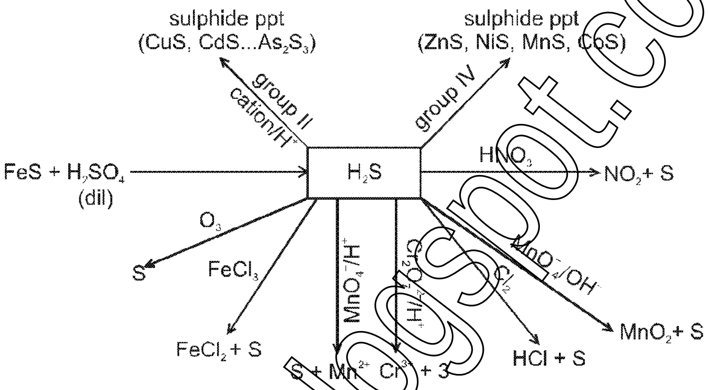
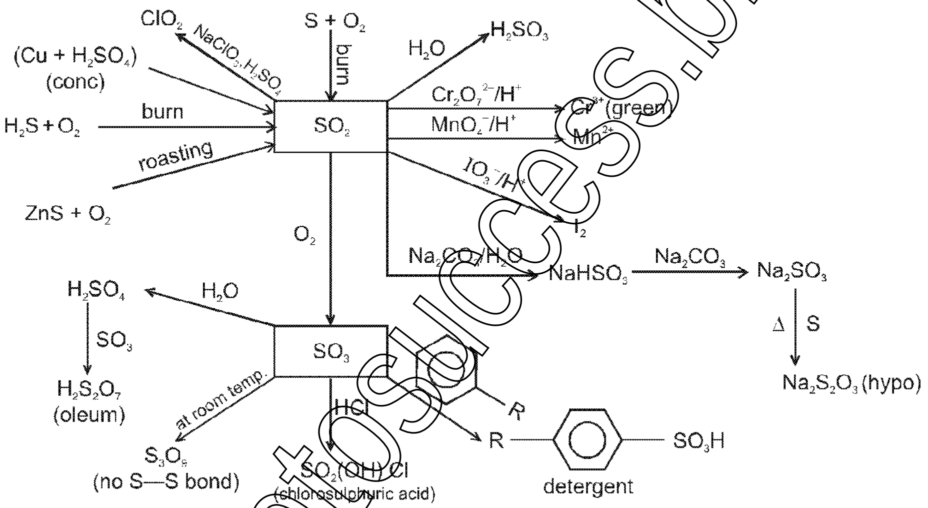
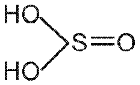
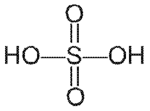
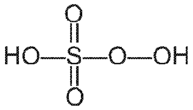
OXYGEN (O_2) AND ITS COMPOUNDS :







Oxo-acids of Sulphur

1.	**Suplhurous**	**acid series**		
	(a) H_2SO_3	S (IV)	sulphurous acid	
2.	**Sulphuric**	**acid series**		
	(a) H_2SO_4	S (VI)	sulphuric acid	
3.	**Peroxo**	**acid series**		
	(a) H_2SO_5	S (VI)	peroxomonosulphuric acid Caro, acid)	

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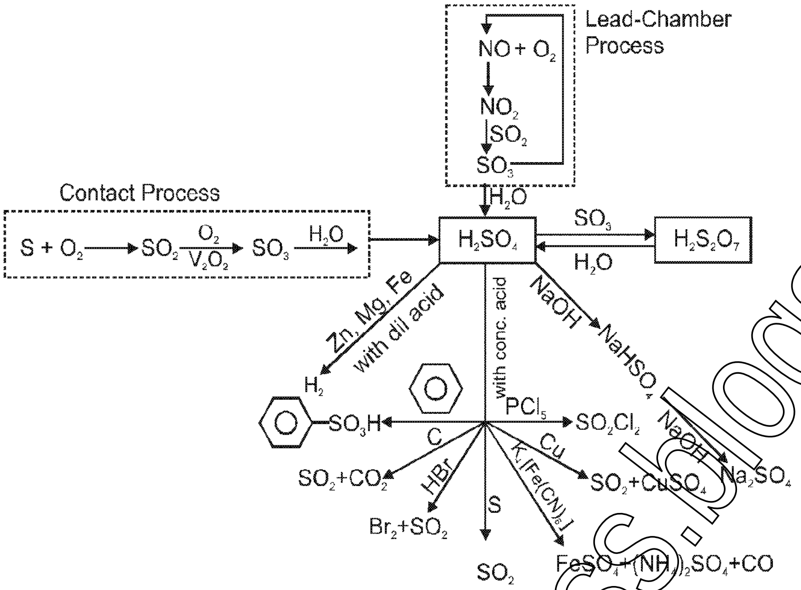

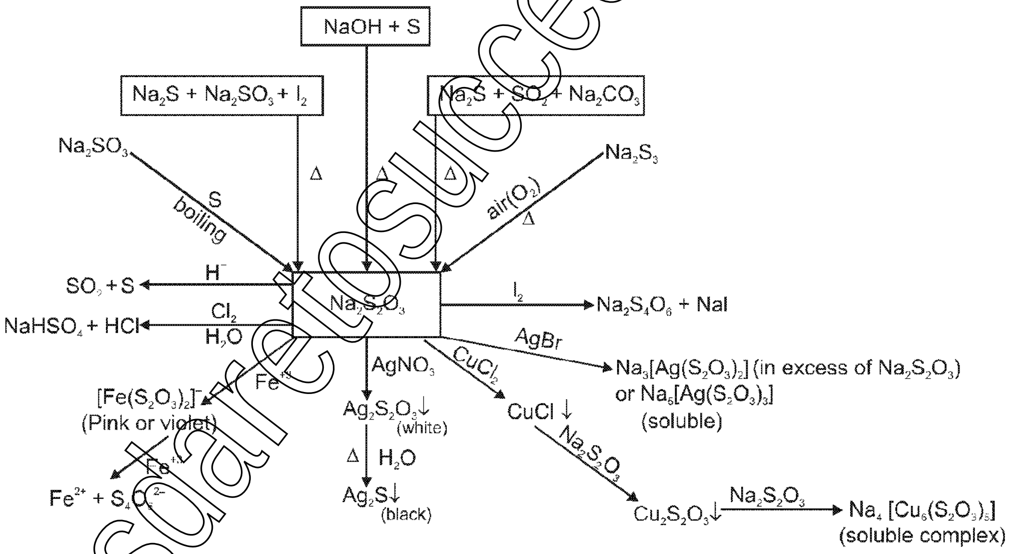

(E) GROUP 17 ELEMENTS : THE HALOGEN FAMILY

Fluorine, chlorine, bromine, iodine and astatine are members of Group 17.

Electronic Configuration : $ns^2 np^5$

Atomic and Ionic Radii

The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge .

Physical Properties

Fluorine and chlorine are gases, bromine is a liquid whereas iodine is a solid. Their melting and boiling points steadily increase with atomic number. The X-X bond disassociation enthalpies from chlorine onwards show the expected trend : Cl – Cl > Br – Br > F – F > I – I.

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Chemical Properties

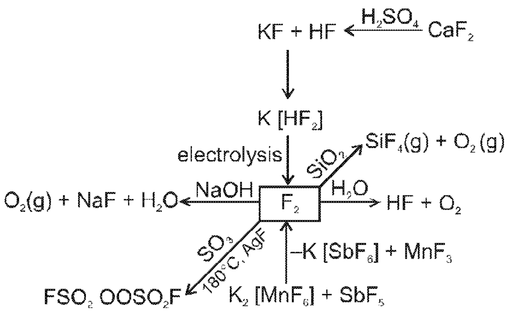
Oxidation states and trends in chemical reactivity

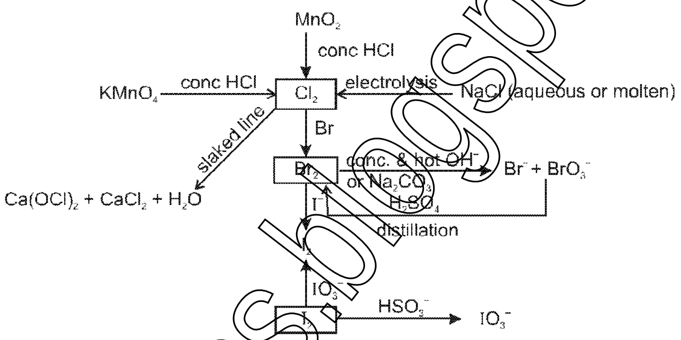
All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit + 1, + 3, + 5 and + 7 oxidation states also.

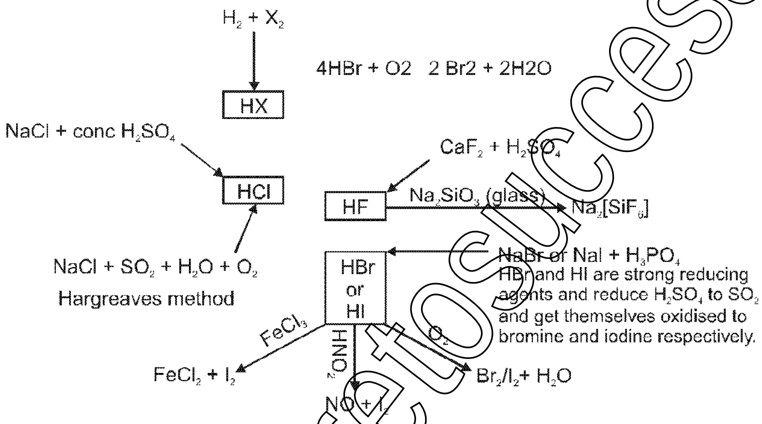
$2F_2(g) + 2H_2O(\ell) \rightarrow 4H^+(aq) + 4F^-(aq) + O_2(g)$

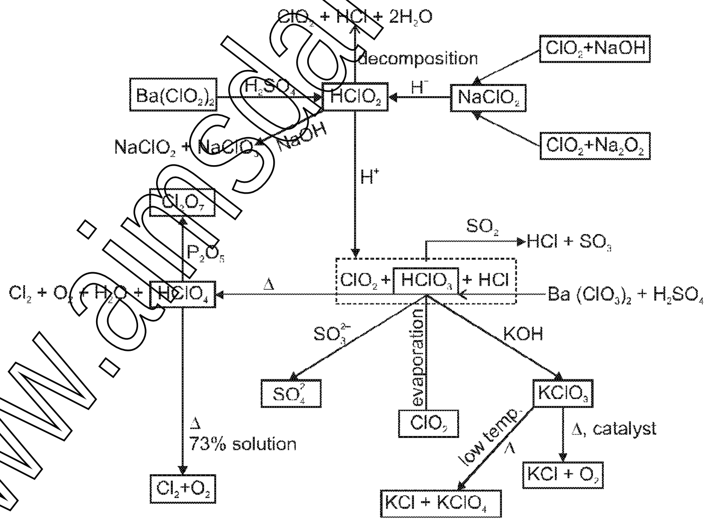
$X_2(g) + H_2O(\ell) \rightarrow HX(aq) + HOX(aq)$; (where X = Cl or Br)

$4I^-(aq) + 4H^+(aq) + O_2(g) \rightarrow 2I_2(s) + 2H_2O(\ell)$









* $2HgO + 2Cl_2 + H_2O \longrightarrow Hg_2OCl_2$ (Oxychloride of mercury) + 2HClO

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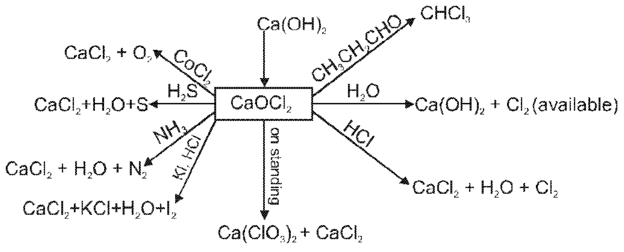
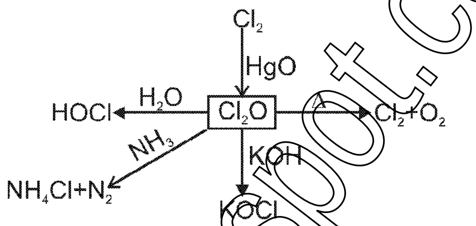
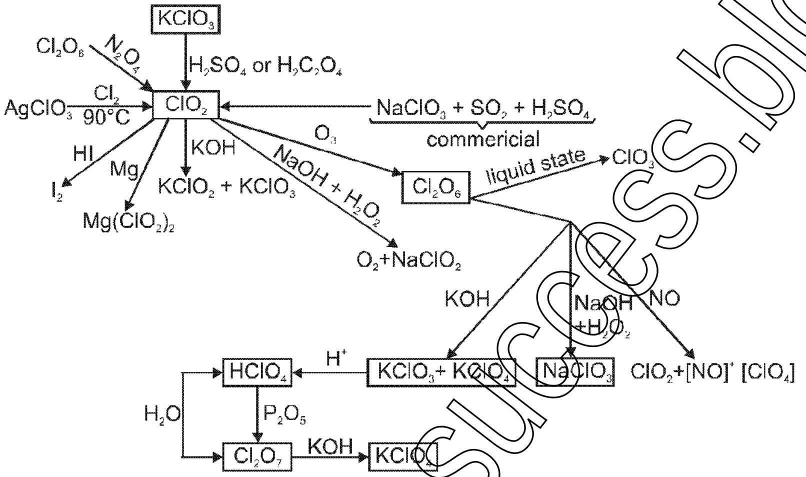


*The composition of bleaching powder is Ca(OCl)2. CaCl2. Ca(OH)2. 2H2O.





(F) GROUP 18 ELEMENTS : (THE ZERO GROUP FAMILY)

helium, neon, argon, krypton , xenon and radon .

- Most abundant element in air is Ar. Order of abundance in the air is Ar > Ne > Kr > He > Xe.

Electronic Configuration : ns^2np^6

Atomic Radii

Atomic radii increase down the group with increase in atomic number.

Physical properties

All the noble gases are mono-atomic. They are colourless, and tasteless. They are sparingly soluble in water. They have very low melting and boiling points because the only type of interatomic interaction in these elements is weak dispersion forces,.

Chemical Properties :

In general, noble gases are least reactive. Their inertness to chemical reactivity is attributed to the following reasons:

(i) The noble gases except helium ($1s^2$) have completely filled ns^2 np^6 electronic configuration in their valence shell.

(ii) They have high ionisation enthalpy and more positive electron gain enthalpy.

The reactivity of noble gases has been investigated occasionally ever since their discovery, but all attempt to

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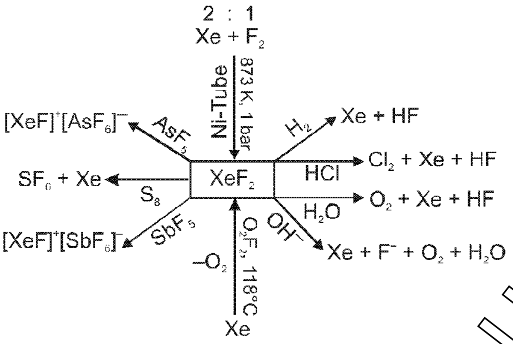
force them to react to form the compounds were unsuccessful for quite a few years. In March 1962, Neil Bartlett, then at the University of British Columbia, observed the reaction of a noble gas. First , he prepared a red compound which is formulated as $O_2^+ PtF_6^-$. He , then realised that the first ionisation enthalpy of molecular oxygen (1175 kJ mol $^{-1}$) was almost identical with that xenon (1170 kJ mol $^{-1}$). He made efforts to prepare same type of compound with $Xe^+ PtF_6^-$ by mixing PtF_6 and Xenon. After this discovery, a number of xenon compounds mainly with most electronegative elements like fluorine and oxygen, have been synthesised.

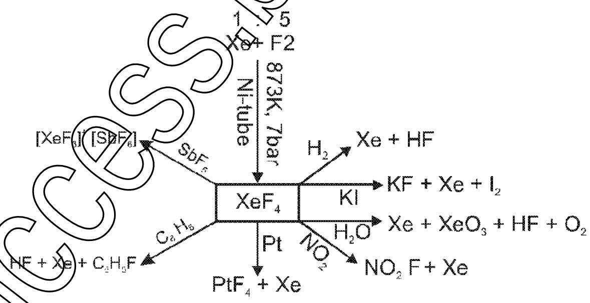
- If Helium is compressed and liquified it forms He(I) liquid at 4.2 K. This liquid is a normal liquid like any other liquid. But if it is further cooled then He(II) is obtained at 2.2 K, which is known as super fluid, because it is a liquid with properties of gases. It climbs through the walls of the container & comes out. It has very high thermal conductivity & very low viscosity.

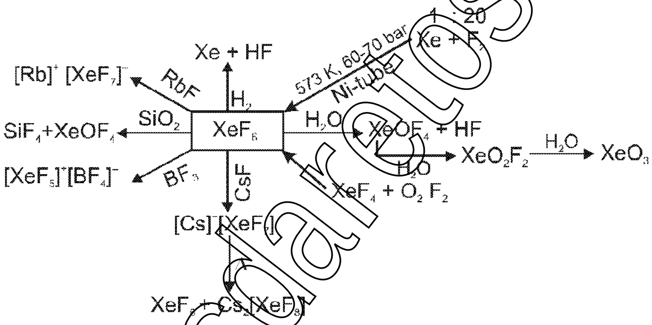
CLATHERATE COMPOUNDS :

During the formation of ice Xe atoms will be trapped in the cavities (or cages) formed by the water molecules in the crystal structure of ice. Compounds thus obtained are called clatherate compounds.

Clathrate provides a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.







d-BLOCK ELEMENTS & THEIR COMPOUNDS

The general electronic configuration of d-block elements is (n–1) d^{1-10} ns^{0-2} , where n is the outer most shell.

General trends in the chemistry of transition elements.

Metallic character :

Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn,Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.

The transition elements (with the exception of Zn, Cd and Hg) are very much hard and have low volatility.

Melting and boiling points :

The melting and boiling points of the transition series elements are gernerally very high.

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Density :

The atomic volumes of the transition elements are low compared with the elements of group 1 and 2. This is because the increased nuclear charge is poorly screened the transition metals are high.

Oxidation states :

Most of transition elements show variable oxidation states. Participation of inner (n – 1) d-electrons in addition to outer ns-electrons because, the energies of the ns and (n – 1) d-subshells are nearly same.

Different oxidation states of first transition series.

Element	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

Characteristics of Oxides and Some Ions of V and Cr

O.S.	Oxide/ Hydroxide	Behaviour	Ion	Name of Ion	Colour of ion
+2	VO	basic	V^{2+}	vanadium (II) (vanadous)	violet
+3	V_2O_5	basic	V^{3+}	vanadium (III) (vanadic)	green
+4	VO_2	amphoteric	VO^{2+}	oxovanadium (IV) (vanadyl)	blue
			$V_4O_9^{2}$	hypovanadate (vanadite)	brown
+5	V_2O_5	amphoteric	VO_2^{+} VO_4^{3-}	dioxovanadium (V) orthovanadate	yellow colourless
+2	CrO $Cr(OH)_2$	basic	Cr^{2+}	chromium (II) (chromous)	light blue
+2	CrO $Cr(OH)_2$	basic	Cr^{2+}	chromium (II) (chromous)	light blue
+3	Cr_2O_3 $Cr(OH)_3$	amphoteric	Cr^{3+} $Cr(OH)^{-}$	chromium (III) chromic chromite	violet green
+5	CrO_3 $CrO_2(OH)_2$ $H_2Cr_2O_7$	acidic	CrO_4^{2-} $Cr_2O_7^{2-}$	chromate dichromate	yellow orange

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Standard electrode potentials :

The value of ionisation enthalpies gives information regarding the thermodynamic stability of the transition metal compounds in different oxidation states. Smaller the ionisation enthalpy of the metal, the stable is its compound.

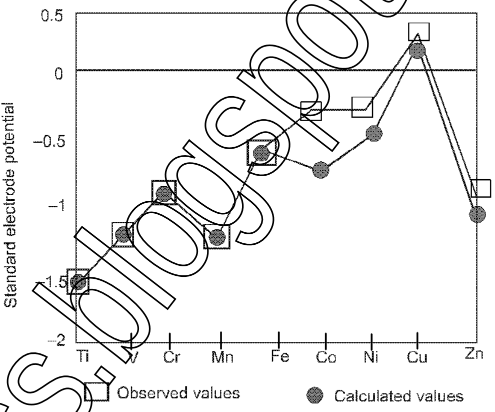
Electrode potentials :

In addition to ionisation enthalpy, the other factors such as enthalpy of sublimation, hydration enthalpy, ionisation enthalpy etc. determine the stability of a particular oxidation state in solution.

The overall energy change is

$$\Delta H = \Delta_{sub}H^{\ominus} + IE + \Delta_{hyd}H$$

The smaller the values of total energy change for a particular oxidation state in aqueous solution, greater will be the stability of that oxidation state. The electrode potentials are a measure of total energy change. Qualitative, the stability of the transition metal ions in different oxidation states can be determined on the basis of electrode potential data. The lower the electrode potential i.e., more negative the standard reduction potential of the electrode, the more stable is the oxidation state of the transition metal in the aqueous solution.

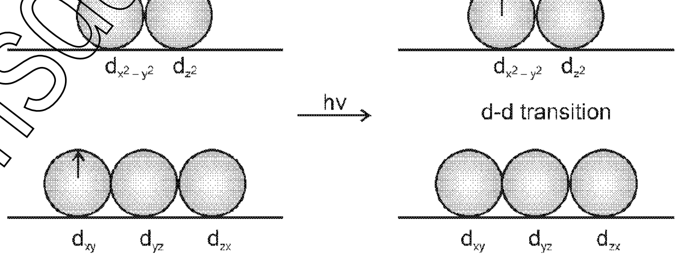


Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of M^{II} to M

Element (M)	Δ_aHq (M)	$\Delta_fH_1^{\theta}$	$\Delta_1H_2^{\theta}$	$\Delta_{hyd}H^{\theta}$ (M^{2+})	E^{θ} /V
Ti	469	661	1310	-1866	-1.63
V	515	648	1370	-1895	-1.18
Cr	398	653	1590	-1925	-0.90
Mn	279	716	1510	-1862	-1.18
Fe	418	762	1560	-1998	-0.44
Co	427	757	1640	-2079	-0.28
Ni	431	736	1750	-2121	-0.25
Cu	339	745	1960	-2121	0.34
Zn	130	908	1730	-2059	-0.76

Formation of Coloured Ions :

Most of the compounds of transition metals are coloured in the solid form or solution form. The colour of the compounds of transition metals may be attributed to the presence of incomplete (n – 1) d-subshell.



The excess of other colours constituting white light are transmitted and the compound appears coloured. The observed colour of a substance is always complementary colour of the colour which is absorbed by the substance.

Magnetic Properties :

(i) **Paramagnetic substances :** The substances which are attracted by magnetic field are called paramagnetic substances.

(ii) **Diamagnetic substances :** The substances which are repelled by magnetic field are called diamagnetic substances. The 'spin only' magnetic moment can be calculated from the relation :

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

where n is the number of unpaired electrons and μ is magnetic moment in Bohr magneton (BM) units.

The paramagnetism first increases in any transition series and than decreases. The maximum paramagnetism is observed around the middle of the series (as contains maximum number of unpaired electrons).

Formation of Interstitial Compounds :

Transition metals form intersitial compounds with elements such as hydrogen, boron, carbon and nitrogen.

Catalytic properties :

Many transition metals and their compounds act as good catalysts for various reactions. Of these, the use of Fe, Co, Ni, V, Cr, Mn, Pt, etc. are very common.

(i) The catalytic property of transition metals is due to their tendency to form reaction intermediates with suitable reactants. These intermediates give reaction paths of lower activation energy and, therefore, increase the rate of the reaction.

(ii) In some cases, the transition metal catalysts provide a suitable large surface area for the adsorption of the reactant. This increases the concentration of the reactants at the catalyst surface and also weakens the bonds in the reactant molecules. Consequently, the activation energy gets lowered.

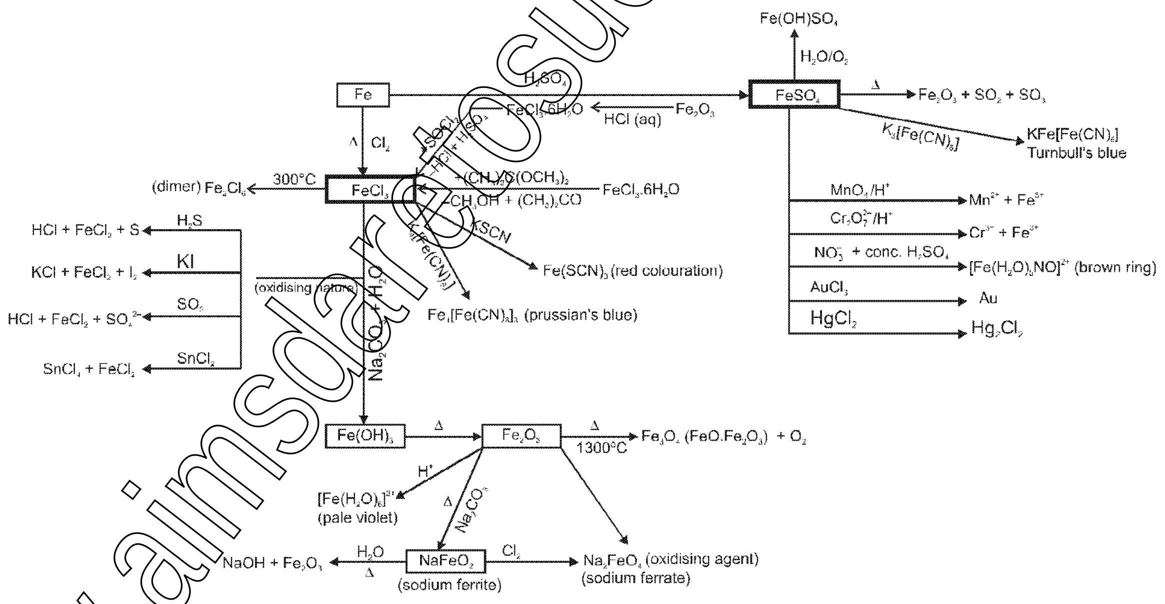
(iii) In some cases, the transition metal ions can change their oxidation states and become more effective as catalysts.

Alloy Formation :

Alloys are hard, have high melting points and are more resistant to corrosion than parent metals.

d-BLOCK METAL COMPOUNDS :

1. Hydrated Ferrous Sulphate ($FeSO_4 \cdot 7H_2O$), Ferric chloride ($FeCl_3$) and iron (III) oxide (Fe_2O_3)



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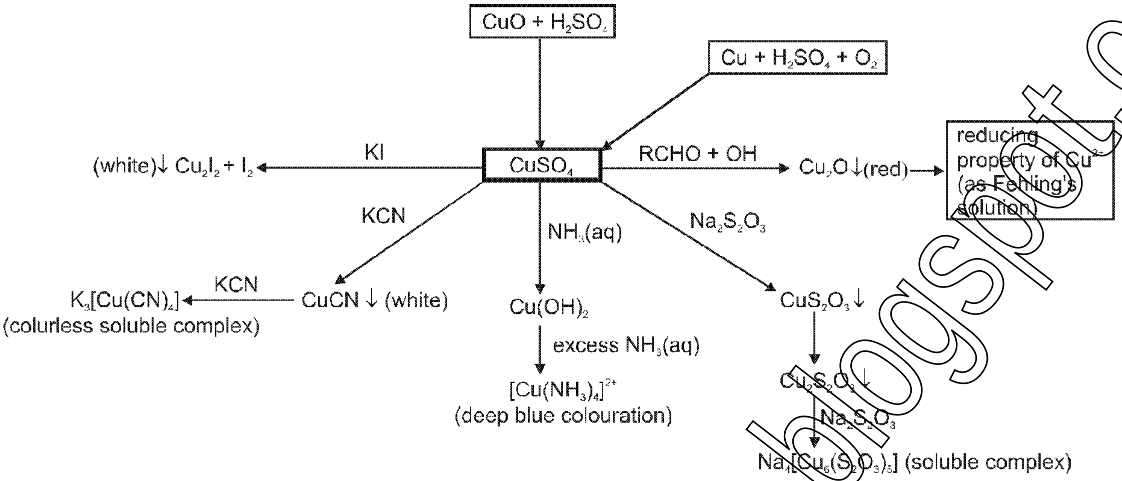
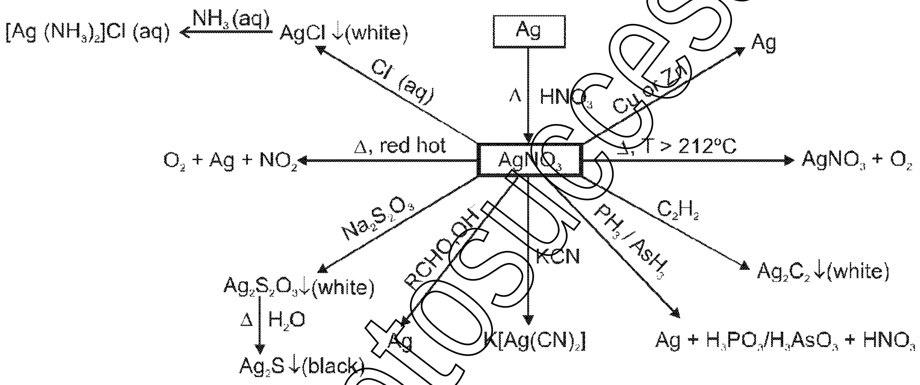
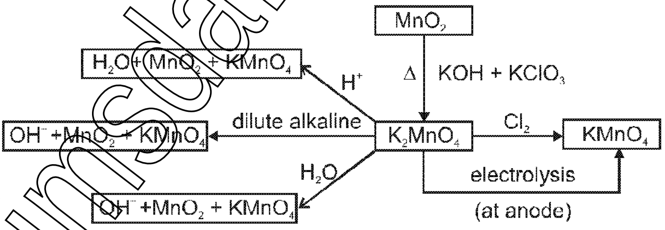
2. Hydrated copper sulphur ($CuSO_4$, $5H_2O$) :



3. Silver nitrate ($AgNO_3$) :



4. Potassium permanganate ($KMnO_4$) :



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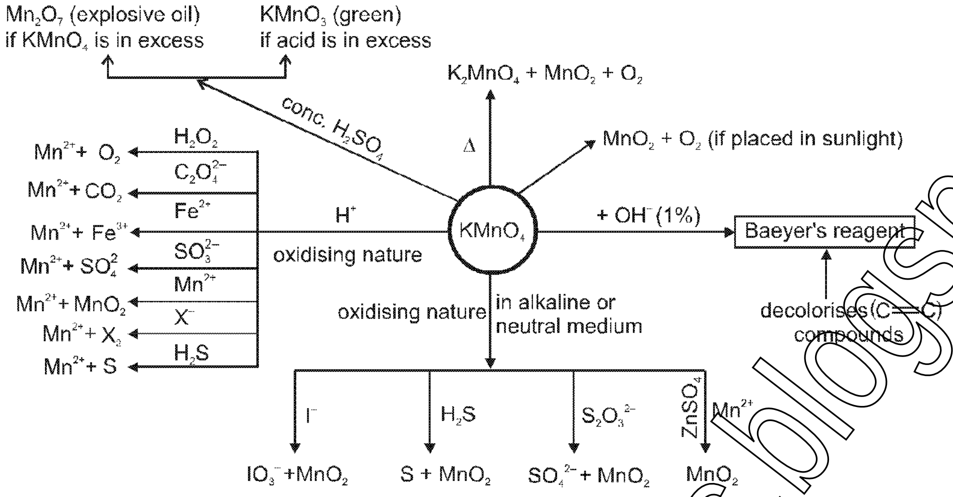
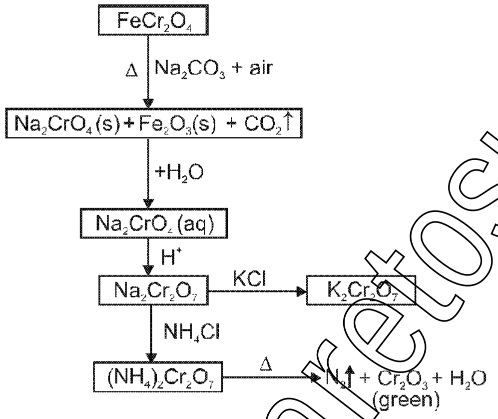
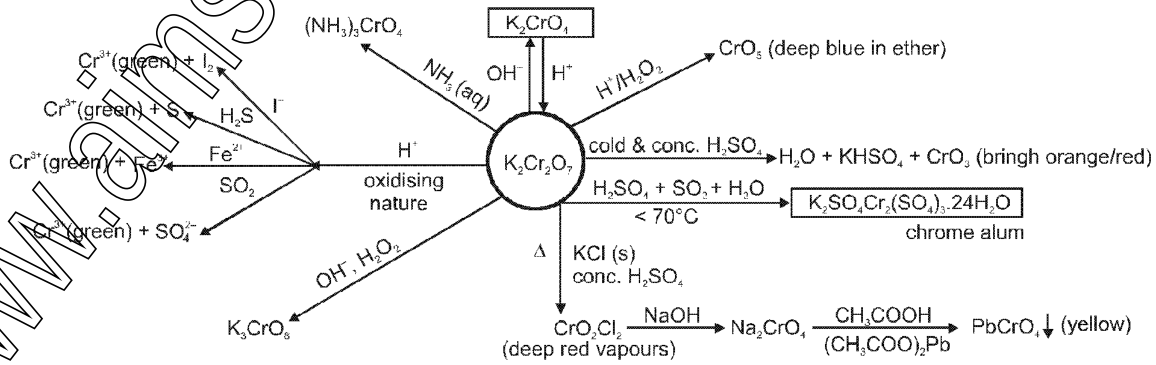


5. Potassium dichromate (K_2CrO_7) :





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QUALITATIVE ANALYSIS

Charcoal Cavity Test :

Observation		Inference
Incrustation or Residue	**Metallic bead**	
Yellow when hot, white when cold	None	Zn^{2+}
Brown when hot, yellow when cold	Grey bead which marks the paper	Pb^{2+}
No characteristic residue	Red beads or scales	Cu^{2+}
White residue which glows on heating	None	$Ba^{2+}, Ca^{2+}, Mg^{2+}$
Black	None	Nothing definite–generally coloured salt

Cobalt Nitrate Test :

S.No.	Metal	Colour of the mass
1.	Zinc	Green
2.	Aluminium	Blue
3.	Magnesium	Pink
4.	Tin	Bluish - green

Flame test :

Colour of Flame	Inference
Crimson Red / Carmine Red	Lithium
Golden yellow	Sodium
Violet/Lilac	Potassium
Brick red	Calcium
Crimson	Strontium
Apple Green/Yellowish Green	Barium
Green with a Blue centre/Greenish Blue	Copper

Borax Bead test :

Metal	Colour in oxidising flame		Colour in reducing flame	
	When Hot	**When Cold**	**When Hot**	**When Cold**
Copper	Green	Blue	Colourless	Brown red
Iron	Brown yellow	Pale yellow/Yellow	Bottle green	Bottle green
Chromium	Yellow	Green	Green	Green
Cobalt	Blue	Blue	Blue	Blue
Manganese	Violet/Amethyst	Red/Amethyst	Grey/Colourless	Grey/Colourless
Nickel	Violet	Brown/Reddish brown	Grey	Grey

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Analysis of ANIONS (Acidic Radicals) :

(a) DILUTE SULPHURIC ACID/DILUTE HYDROCHLORIC ACID GROUP :

1. CARBONATE ION (CO_3^{2-}) :

- Dilute H_2SO_4 test : A colourless odourless gas is evolved with brisk effervescence.

$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2\uparrow$

- Lime water/Baryta water ($Ba(OH)_2$) test :

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow$ (milky) $+ H_2O$

$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$ (soluble) $\xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2$

2. SULPHITE ION (SO_3^{2-}) :

- **Dilute H_2SO_4 test :**

$CaSO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + SO_2\uparrow$; SO_2 has suffocating odour of burning sulphur.

- **Acidified potassium dichromate test :** The filter paper dipped in acidified $K_2Cr_2O_7$ turns green.

$Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+}$ (green) $+ 3SO_4^{2-} + H_2O$.

- **Barium chloride/Strontium chloride solution :**

$SO_3^{2-} + Ba^{2+}/Sr^{2+} \longrightarrow BaSO_3/SrSO_3\downarrow$ (white).

☞ White precipitate dissolves in dilute HCl. $BaSO_3\downarrow + 2H^+ \longrightarrow Ba^{2+} + SO_2\uparrow + H_2O$.

3. SULPHIDE ION (S^{2-}) :

- **Dilute H_2SO_4 test :** Pungent smelling gas like that of rotten egg is obtained.

$S^{2-} + 2H^+ \longrightarrow H_2S\uparrow$

- **Lead acetate test :** $(CH_3COO)_2Pb + H_2S \longrightarrow PbS\downarrow$ (black) $+ 2CH_3COOH$.
- **Sodium nitroprusside test :** Purple coloration is obtained.

$S^{2-} + [Fe(CN)_5(NO)]^{2-} \longrightarrow [Fe(CN)_5NOS]^{4-}$ (violet).

- **Cadmium carbonate suspension/ Cadmium acetate solution :**

$Na_2S + CdCO_3 \longrightarrow CdS\downarrow$ (Yellow) $+ Na_2CO_3$

4. NITRITE ION (NO_2^-) :

- **Dilute H_2SO_4 test :**

$NO_2^- + H^+ \longrightarrow HNO_2$; $(2HNO_2 \longrightarrow H_2O + N_2O_3)$;
$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$; $2NO + O_2 \longrightarrow 2NO_2\uparrow$

- **Starch iodide test :**

$2NO_2^- + 3I^- + 4CH_3COOH \longrightarrow I_3^- + 2NO\uparrow + 4CH_3COO^- + 2H_2O$
Starch $+ I_3^- \longrightarrow$ Blue (starch iodine adsorption complex)

5. ACETATE ION (CH_3COO^-) :

- **Dilute H_2SO_4 test :** $(CH_3COO)_2Ca + H_2SO_4 \longrightarrow 2CH_3COOH$ (vinegar like smell) $+ CaSO_4$
- **Neutral ferric chloride test :**

$6CH_3COO^- + 3Fe^{3+} + 2H_2O \longrightarrow [Fe_3(OH)_2(CH_3COO)_6]^+$ (deep red/ blood red colouration) $+ 2H^+$
$[Fe_3(OH)_2(CH_3COO)_6]^+ + 4H_2O \xrightarrow{Boil} 3Fe(OH)_2CH_3COO\downarrow$ (brownish red) $+ 3CH_3COOH + H^+$

(b) CONC . H_2SO_4 GROUP :

1. CHLORIDE ION (Cl^-) :

- **Concentrated H_2SO_4 test :** $Cl^- + H_2SO_4 \longrightarrow HCl$ (colourless pungent smelling gas) $+ HSO_4^-$
- $NH_4OH + HCl \longrightarrow NH_4Cl\uparrow$ (white fumes) $+ H_2O$.
- **Silver nitrate test :** $Cl^- + Ag^+ \longrightarrow AgCl\downarrow$ (white)

☞ White precipitate is soluble in aqueous ammonia and precipitate reappears with HNO_3.

$AgCl + 2NH_4OH \longrightarrow [Ag(NH_3)_2]Cl$ (Soluble) $+ 2H_2O$; $[Ag(NH_3)_2]Cl + 2H^+ \longrightarrow AgCl\downarrow + 2NH_4^+$.

- **Chromyl chloride test :**

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$4Cl^- + Cr_2O_7^{2-} + 6H^+ \text{ (conc.)} \longrightarrow 2CrO_2Cl_2 \text{ (deep red vapours)} + 3H_2O$
$CrO_2Cl_2 + 4OH^- \longrightarrow CrO_4^{2-} + 2Cl^- + 2H_2O$; $CrO_4^{2-} + Pb^{+2} \longrightarrow PbCrO_4 \downarrow \text{ (yellow)}$

2. BROMIDE ION (Br^-) :

- **Concentrated H_2SO_4 test :**
  $2NaBr + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr$; $2HBr + H_2SO_4 \longrightarrow Br_2 \uparrow \text{ (reddish-brown)} + 2H_2O + SO_2$
- **Silver nitrate test :** $NaBr + AgNO_3 \longrightarrow AgBr \downarrow$ (pale yellow) $+ NaNO_3$

☞ Yellow precipitate is partially soluble in dilute aqueous ammonia but readily dissolves in concentrated ammonia solution. $AgBr + 2NH_4OH \longrightarrow [Ag(NH_3)_2]\,Br + H_2O$

- **Chlorine water test (organic layer test) :**
  $2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2 \uparrow$.
  $Br_2 + CHCl_3 / CCl_4 \longrightarrow Br_2$ dissolve to give reddish brown colour in organic layer.

3. IODIDE ION (I^-) :

- **Concentrated H_2SO_4 test :** $2NaI + H_2SO_4 \longrightarrow Na_2SO_4 + 2HI$
  $2HI + H_2SO_4 \longrightarrow I_2 \uparrow$ (pungent smelling dark violet) $+ 2H_2O + SO_2$
- **Starch paper test :** Iodides are readily oxidised in acid solution to free iodine; the free iodine may than be identified by deep blue colouration produced with starch solution.
  $3I^- + 2NO_2^- + 4H^+ \longrightarrow I_3^- + 2NO \uparrow + 2H_2O$.
- **Silver nitrate test :** Bright yellow precipitate is formed.
  $I^- + Ag^+ \longrightarrow AgI \downarrow$

☞ Bright yellow precipitate is insoluble in dilute aqueous ammonia but is partially soluble in concentrated ammonia solution.

- **Chlorine water test (organic layer test) :**
  $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$
  $I_2 + CHCl_3 \longrightarrow I_2$ dissolves to give violet colour in organic layer.

4. NITRATE ION (NO_3^-) :

- **Concentrated H_2SO_4 test :** Pungent smelling reddish brown vapours are evolved.
  $4NO_3^- + 2H_2SO_4 \longrightarrow 4NO_2 \uparrow + O_2 + 2SO_4^{2-} + 2H_2O$

☞ Addition of bright copper turnings or paper pellets intensifies the evolution of reddish brown gas.
$2NO_3^- + 4H_2SO_4 + 3Cu \longrightarrow 3Cu^{2+} + 2NO \uparrow + 4SO_4^{2-} + 4H_2O$; $2NO \uparrow + O_2 \longrightarrow 2NO_2 \uparrow$
$4\,C \text{ (paper pellet)} + 4HNO_3 \longrightarrow 2H_2O + 4NO_2 + 4CO_2$.

- ***Brown ring test :***
  $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO \downarrow + 4SO_4^{2-} + 4H_2O$.
  $Fe^{2+} + NO \uparrow + 5H_2O \longrightarrow [Fe^{I}(H_2O)_5\,NO^+]^{2+}$ (brown ring).

3. Miscellaneous Group :

1. SULPHATE ION (SO_4^{2-}) :

- ◇**Barium chloride test :** $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 \downarrow \text{(white)} + 2NaCl$.

☞ White precipitate is insoluble in warm dil. HNO_3 as well as HCl but moderately soluble in boiling concentrated hydrochloric acid.

- **Lead acetate test :** $Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow PbSO_4 \downarrow \text{(White)} + 2CH_3COONa$

☞ White precipitate soluble in excess of hot ammonium acetate.
$PbSO_4 + 2CH_3COONH_4 \longrightarrow (CH_3COO)_2Pb \text{ (soluble)} + (NH_4)_2SO_4$

2. PHOSPHATE ION (PO_4^{3-}) :

- **Ammonium molybdate test :**

$Na_2HPO_4 \text{ (aq)} + 12(NH_4)_2MoO_4 + 23HNO_3 \rightarrow (NH_4)_3PMo_{12}O_{40} \downarrow \text{ (canary yellow)} + 2NaNO_3 + 21NH_4NO_3 + 12H_2O$

ANALYSIS OF CATIONS

1. AMMONIUM ION (NH_4^+) :

$2NH_3 + Mn^{2+} + H_2O_2 + H_2O \longrightarrow MnO(OH)_2 \downarrow$ (brown) + $2NH_4^+$

Nessler's reagent (Alkaline solution of potassium tetraidomercurate(II) :

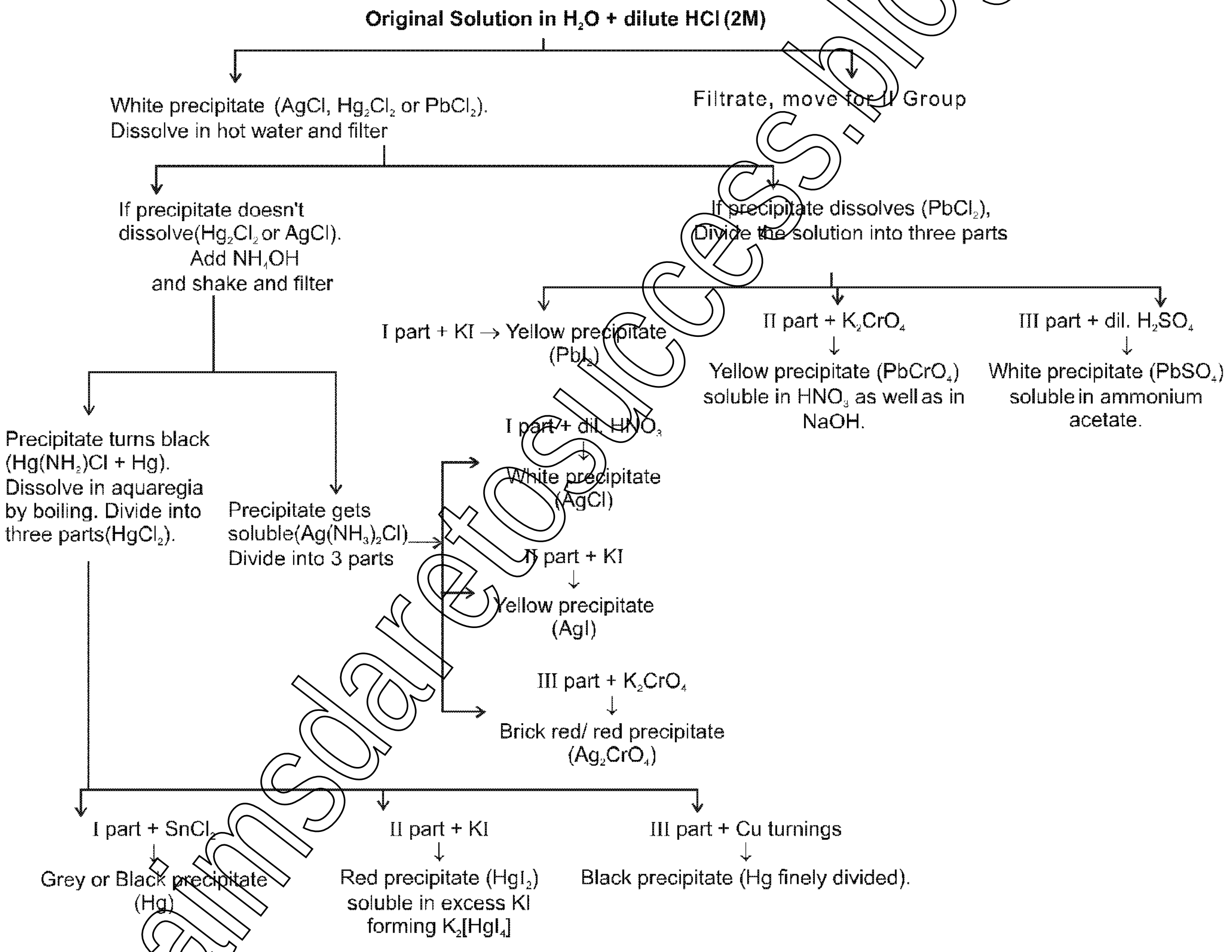
$NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \longrightarrow HgO\,Hg\,(NH_2)I \downarrow$ (brown) + $7I^- + 3H_2O$

$3NH_4^+ + [Co(NO_2)_6]^{3-} \longrightarrow (NH_4)[Co(NO_2)_6]\downarrow$ (yellow)

$2NH_4^+ + [PtCl_6]^- \longrightarrow (NH_4)_2\,[PtCl_6]\downarrow$ yellow

$NH_4^+ + HC_4H_4O_6^- \longrightarrow NH_4\,HC_4H_4O_6\downarrow$

Ist GROUP (Pb^{2+}, Hg_2^{2+}, Ag^+) :



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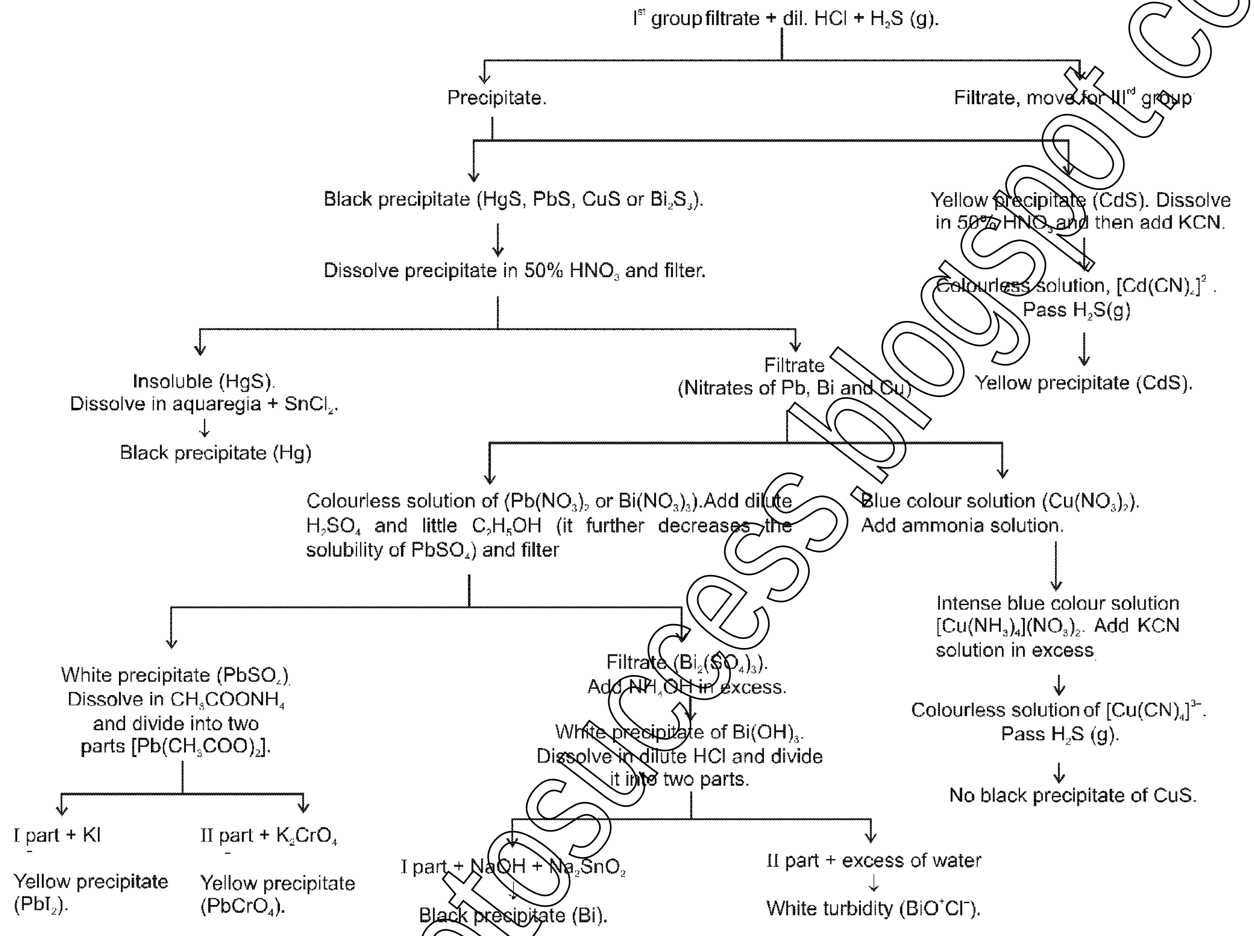
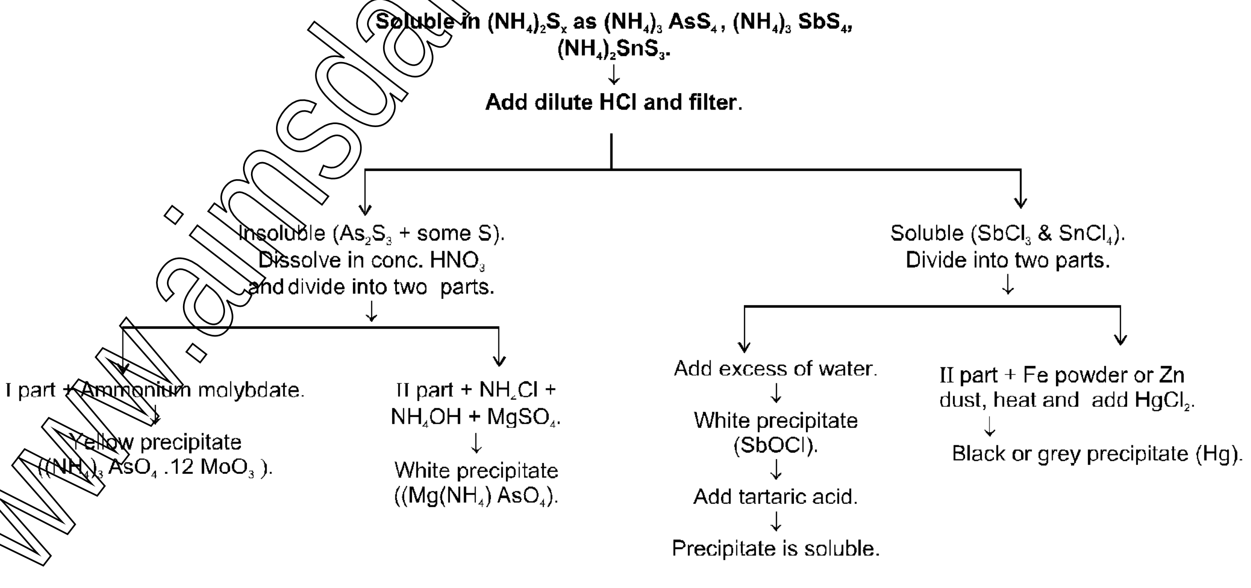
IIA Group (Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+})



IIB Group (As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+})



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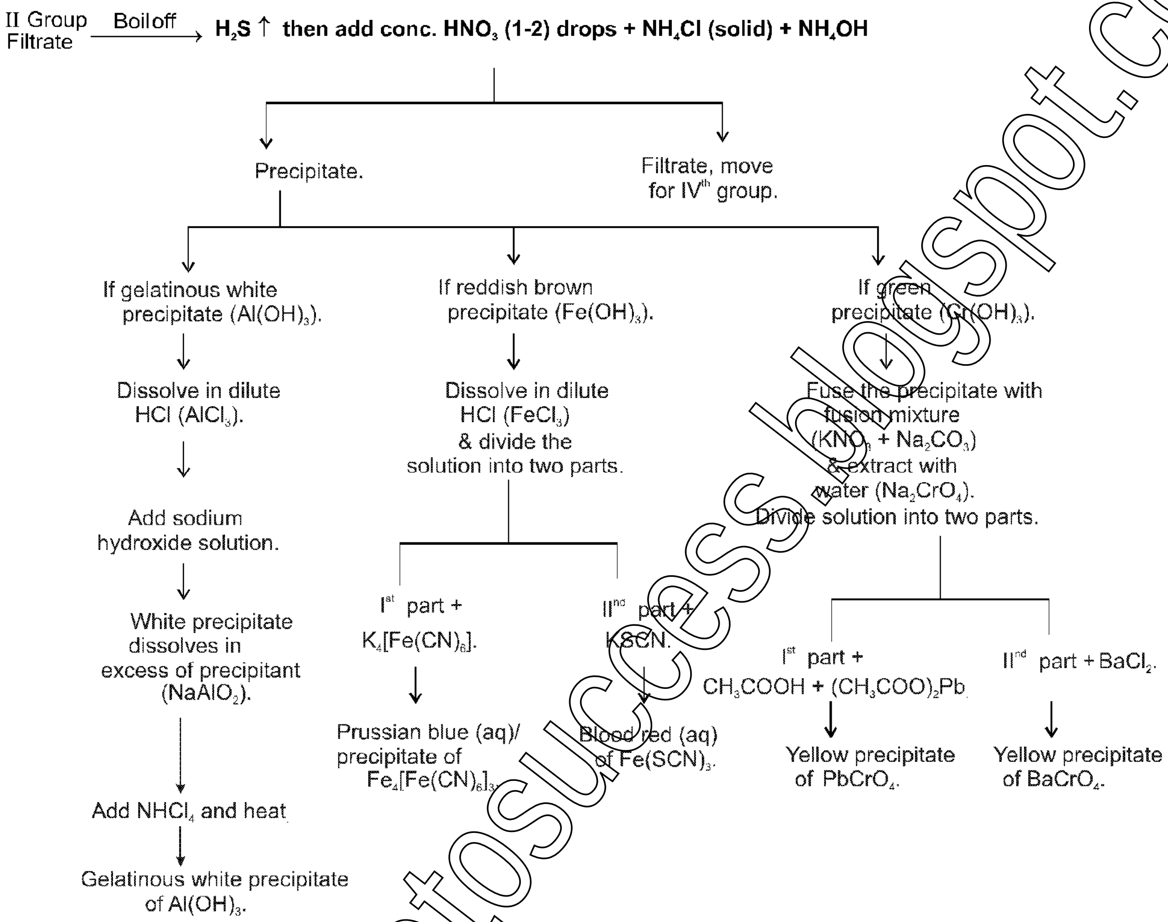
IIIrd Group (Al^{+3}, Cr^{+3}, Fe^{+3})



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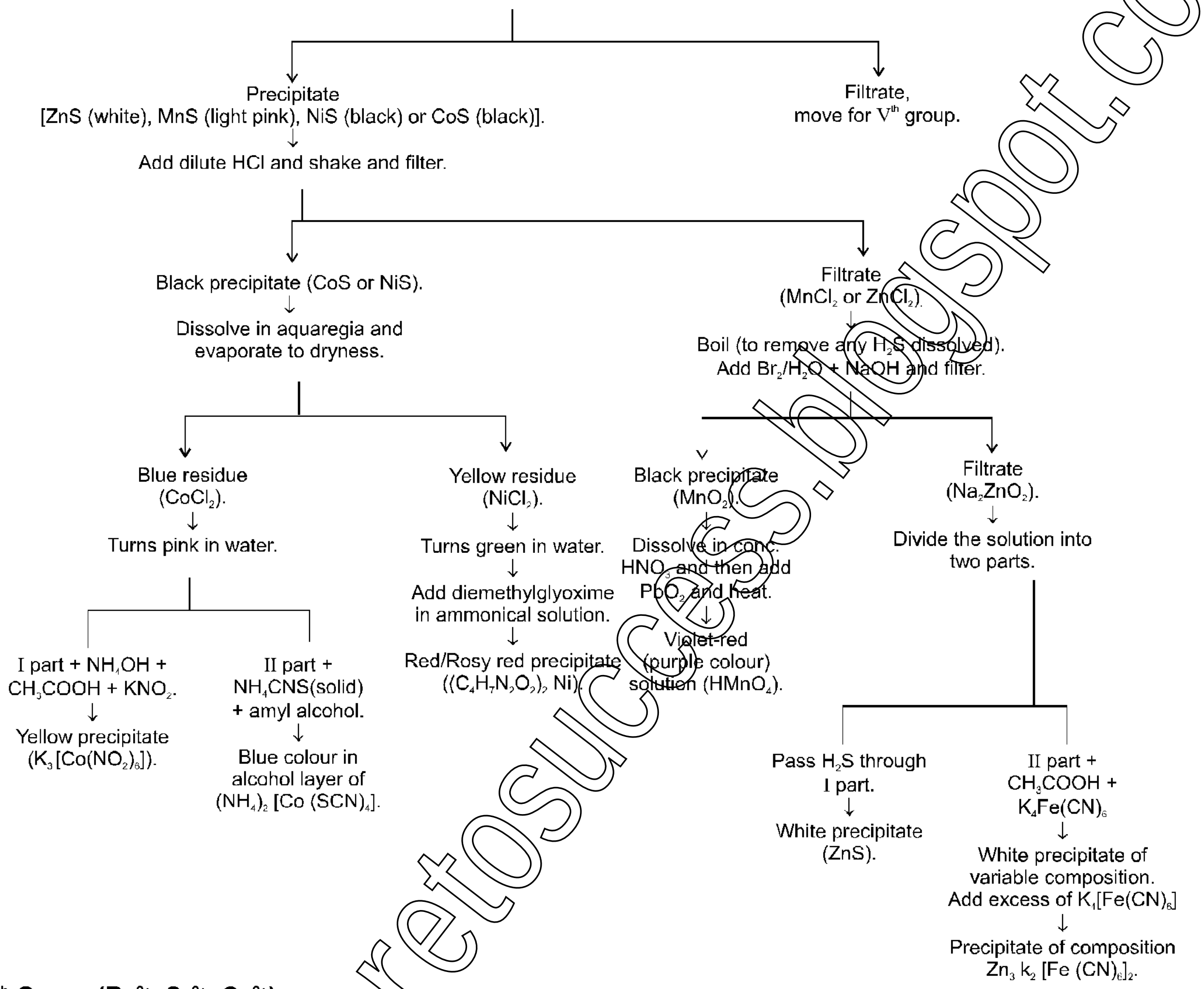
IVth GROUP (Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}) :

III Group filtrate + NH_4OH (excess) & NH_4Cl , then pass H_2S



Precipitate [ZnS (white), MnS (light pink), NiS (black) or CoS (black)].
↓
Add dilute HCl and shake and filter.

Black precipitate (CoS or NiS).
↓
Dissolve in aquaregia and evaporate to dryness.

Blue residue ($CoCl_2$).
↓
Turns pink in water.

I part + NH_4OH + CH_3COOH + KNO_2.
↓
Yellow precipitate ($K_3[Co(NO_2)_6]$).

II part + NH_4CNS(solid) + amyl alcohol.
↓
Blue colour in alcohol layer of $(NH_4)_2[Co(SCN)_4]$.

Yellow residue ($NiCl_2$).
↓
Turns green in water.
↓
Add diemethylglyoxime in ammonical solution.
↓
Red/Rosy red precipitate $((C_4H_7N_2O_2)_2Ni)$.

Filtrate ($MnCl_2$ or $ZnCl_2$).
↓
Boil (to remove any H_2S dissolved).
Add Br_2/H_2O + NaOH and filter.

Black precipitate (MnO_2).
↓
Dissolve in conc. HNO_3 and then add PbO_2 and heat.
↓
Violet-red (purple colour) solution ($HMnO_4$).

Filtrate (Na_2ZnO_2).
↓
Divide the solution into two parts.

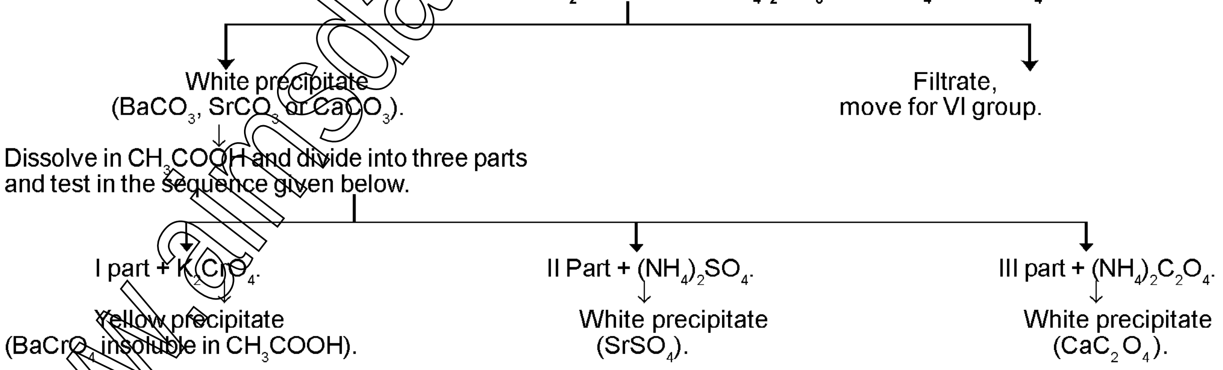
Pass H_2S through I part.
↓
White precipitate (ZnS).

II part + CH_3COOH + $K_4Fe(CN)_6$
↓
White precipitate of variable composition.
Add excess of $K_4[Fe(CN)_6]$
↓
Precipitate of composition $Zn_3K_2[Fe(CN)_6]_2$.

Filtrate, move for Vth group.

Vth Group (Ba^{2+}, Sr^{2+}, Ca^{2+}) :

IV Group filtrate $\longrightarrow$ Boil off H_2S then add $(NH_4)_2CO_3$ (aq), NH_4OH & NH_4Cl (s)



White precipitate ($BaCO_3$, $SrCO_3$ or $CaCO_3$).
↓
Dissolve in CH_3COOH and divide into three parts and test in the sequence given below.

I part + K_2CrO_4.
↓
Yellow precipitate ($BaCrO_4$ insoluble in CH_3COOH).

II Part + $(NH_4)_2SO_4$.
↓
White precipitate ($SrSO_4$).

III part + $(NH_4)_2C_2O_4$.
↓
White precipitate (CaC_2O_4).

Filtrate, move for VI group.

VIth GROUP :

MAGNESIUM ION (Mg^{2+}) :

$$Mg^{2+} + NH_3 + HPO_4^{2-} \longrightarrow Mg(NH_4)PO_4 \downarrow \text{(white)}$$

$$5\,Mg^{2+} + 6\,CO_3^{2-} + 7\,H_2O \longrightarrow 2\,MgCO_3.\,Mg(OH)_2.\,5\,H_2O \downarrow + 2HCO_3^-$$

Titan Yelllow (a water soluble yellow dyestuff) : It is adsorbed by $Mg(OH)_2$ producing a deep red colour or precipitate.

ORGANIC

1. Alkane

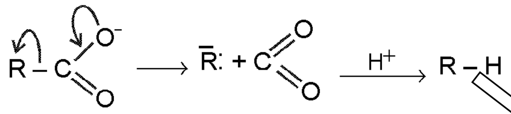
Wurtz reaction :

e.g., $R^1X + R^2X + 2Na \longrightarrow R^1 - R^2 + 2NaX$

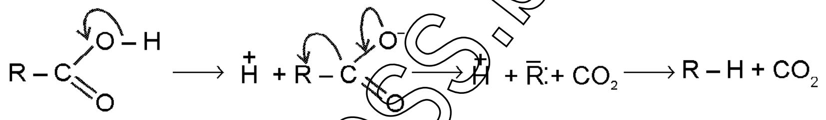
Decarboxylation :

General reaction $RCOONa \xrightarrow{H^+} R-H + Na_2CO_3$

Mechanism



The thermal decarboxylation of free acids may be :



2. Alkyl halide

Nucleophilic substitution Reaction (S_N1, S_N2)

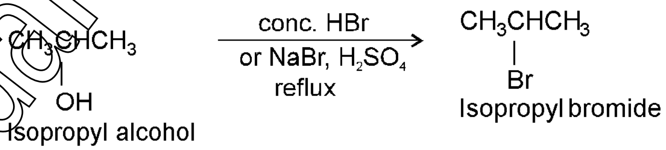
S_N1 reaction : $R-OH + HX \longrightarrow R-X + H_2O$ (R may rearrange)

Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : allyl, benzyl > 3° > 2° > 1° (Carboocation)
Carbocation formed

Mechanism $R-OH \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} \overset{\oplus}{R} \xrightarrow{X^{\ominus}} R-X$

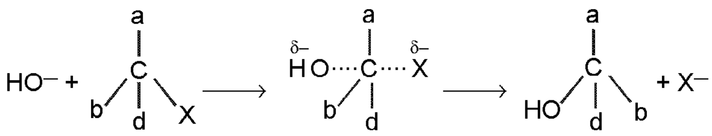
e.g.



$$\underset{\text{Isopropyl alcohol}}{CH_3\underset{OH}{\underset{|}{C}}HCH_3} \xrightarrow[\text{or NaBr, } H_2SO_4 \text{, reflux}]{\text{conc. HBr}} \underset{\text{Isopropyl bromide}}{CH_3\underset{Br}{\underset{|}{C}}HCH_3}$$

S_N2 reaction : Alkylhalide are hydrolysed to alcohol very solwly by water, but rapidly by silver oxide suspended in boiling water.
$RX + KOH \longrightarrow ROH + KX$

Mechanism $HO^- \; R-X \longrightarrow \overset{\delta-}{H}O \cdots R \cdots \overset{\delta-}{X} \longrightarrow HO-R + X^-$



Williamson's synthesis :

It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide (S_N2).

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$$R_1O^- + R^2{-}X \rightleftharpoons R^1\overset{\delta-}{O}\ldots\ldots R^2\ldots\ldots\overset{\delta-}{X} \longrightarrow R^1OR^2 + X^-(g)$$

This method is particularly useful for preparing mixed ethers.

3. Grignard Reagents

$$R^1H + Mg(OH)X \xleftarrow{H_2O} R^1MgX \xrightarrow{R^2OH} R^1H + Mg(OR^2)X$$

The majority of Grignard reactions fall into two groups

(i) Addition of the Grignard reagent to a compound containing a multiple - bond group e.g.

$$>C=O\ ;\ -C\equiv N\ ;\ >C=S;\ —N=O\ ;\ >S=O$$

(ii) Double decompsition with compounds containing an active hydrogen atom or a reactive halogen atom.

$$R^1H + Mg(OH)X \xleftarrow{H_2O} R^1MgX \xrightarrow{R^2OH} R^1H + Mg(OR^2)X$$

Important chemical synthesis by Grignard reagent

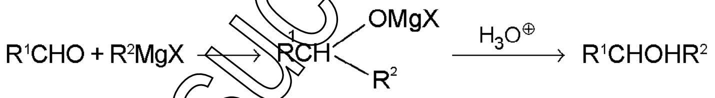
1. **Hydrocarbons :** $RMgBr + H_2O \xrightarrow{H^\oplus} RH + Mg(OH)Br$

$RMgBr + RNH_2 \xrightarrow{H^\oplus} RH + RNHMgBr$

2. **Alcohols :**

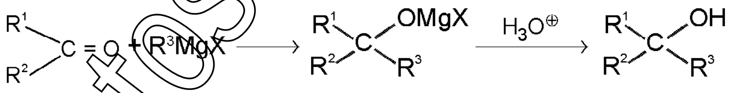
(a) Primary alcohols $RMgX \xrightarrow{O_2} RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H_3O^\oplus} 2ROH$

(b) Secondary alcohols



$R^1CHO + R^2MgX \longrightarrow R^1CH(OMgX)(R^2) \xrightarrow{H_3O^\oplus} R^1CHOHR^2$

(c) Tertiary alcohols :

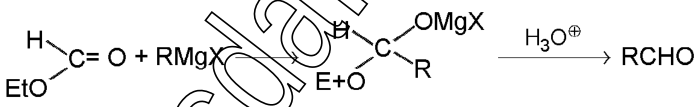


$R^1R^2C=O + R^3MgX \longrightarrow R^1R^2C(OMgX)R^3 \xrightarrow{H_3O^\oplus} R^1R^2C(OH)R^3$

3. **Ethers :**

$R^1OCH_2Cl + R^2MgX \longrightarrow R^1OCH_2R^2 + MgXCl$

4. **Aldehydes :**



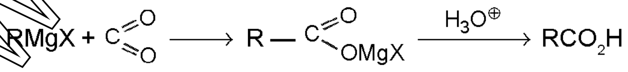
$H(EtO)C=O + RMgX \longrightarrow H(EtO)C(OMgX)R \xrightarrow{H_3O^\oplus} RCHO$

5. **Ketones :**

$R^1C(OC_2H_5)_3 + R^2MgX \longrightarrow R^1R^2C(OC_2H_5)x + Mg(OC_2H_5)x \xrightarrow{H_3O^\oplus} R^1COR^2$

$R^1CN + R^2MgX \longrightarrow R^1R^2C=NMgX \xrightarrow{H_3O^\oplus} \underset{\text{Ketimine}}{[R^1R^2C=NH]} \xrightarrow{H_3O^\oplus} R^1COR^2 + NH_3$

6. **Acids :**



$RMgX + O{=}C{=}O \longrightarrow R—C(=O)OMgX \xrightarrow{H_3O^\oplus} RCO_2H$

7. **Esters :**

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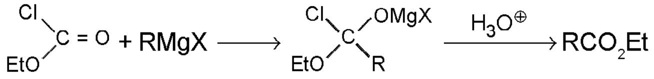


$$Cl(EtO)C{=}O + RMgX \longrightarrow Cl(EtO)C(OMgX)R \xrightarrow{H_3O^{\oplus}} RCO_2Et$$

8. **Alkyl Cyanides :**

$RMgX + (CN)_2 \longrightarrow RCN + Mg(CN)x$

9. **Primary amines :**

$RMgX + RONH_2 \longrightarrow RNHMgX + RH + Mg(OCH_3)Cl \xrightarrow{H_3O^{\oplus}} RNH_2$ (40-90%)

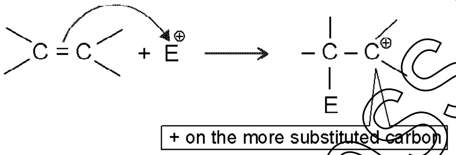
$RMgX + ClNH_2 \longrightarrow RNH_2 + MgxCl$

4. Alkene & Alkyne

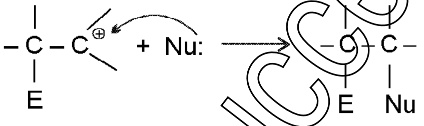
Electrophilic addition reactions :

Mechanism

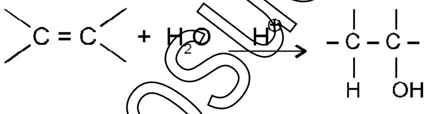
Step 1 : Attack of the electrophile on π bond forms a carbocation.



Step 2 : Attack by a nucleophile gives the product of addition.

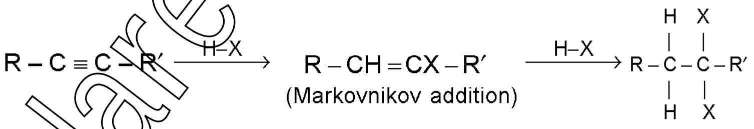


e.g. (a) Addition of water



(Markovnikov orientation)

(b) Addition of hydrogen halides (where HX = HCl, HBr, HI)



$$R-C\equiv C-R' \xrightarrow{H-X} R-CH=CX-R' \xrightarrow{H-X} R-CH_2-CX_2-R'$$

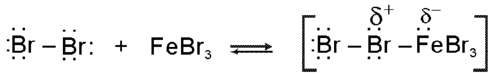
(Markovnikov addition)

5. Aromatic compounds

Electrophilic aromatic substitution :

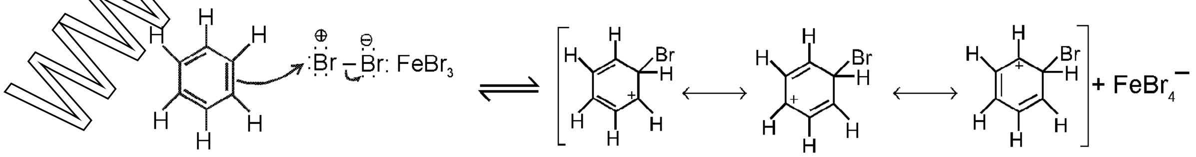
(a) Bromination of Benzene : Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as $FeBr_3$ catalyzes the reaction.

Step 1 : Formation of a stronger electrophile.



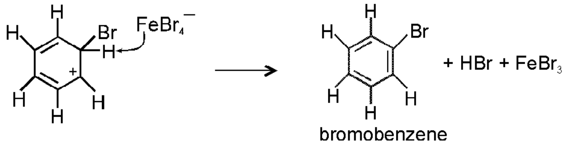
$$:\ddot{Br}-\ddot{Br}: + FeBr_3 \rightleftharpoons \left[:\ddot{Br}-\overset{\delta^+}{\ddot{Br}}-\overset{\delta^-}{Fe}Br_3\right]$$

Step 2 : Electrophilic attack and formation of the sigma complex.

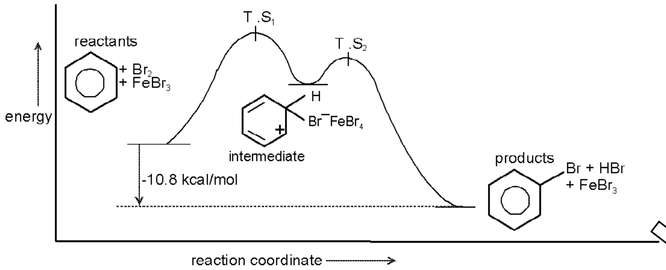


sigma complex

Step :2 Loss of a proton gives the products.

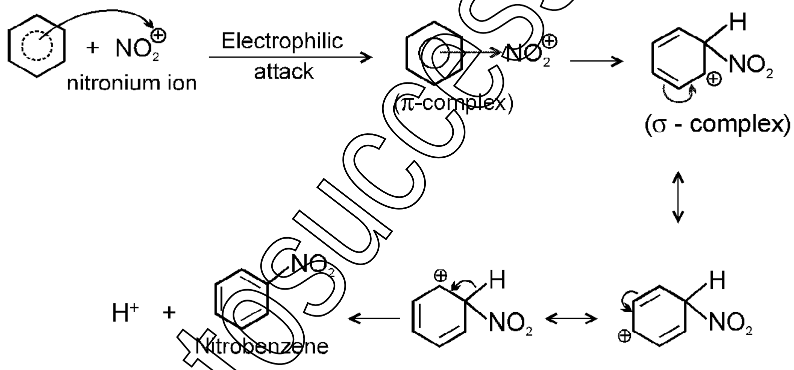


bromobenzene



(b) Nitration

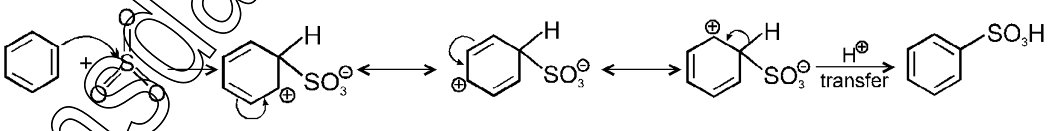
$$H\ddot{O}-NO_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} H_2\underset{\oplus}{O}-NO_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} H_3O^{\oplus} + HSO_4^{\ominus} + {}^{\oplus}NO_2$$



(c) Sulphonation :

The electrophilic reagent, SO_3, attacks the benzene ring to form the intermediate carbocation.

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$$

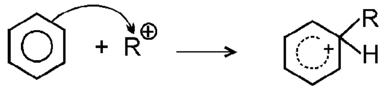


(d) Friedel Craft reaction :

Alkylation mechanism

(i) $R-\ddot{C}l: + AlCl_3 \longrightarrow R-\overset{\delta+}{Cl}-\overset{\delta-}{AlCl_3} \longrightarrow R^{\oplus} + AlCl_4^{\ominus}$

carbocation

(ii) 

σ-complex

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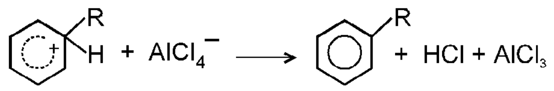
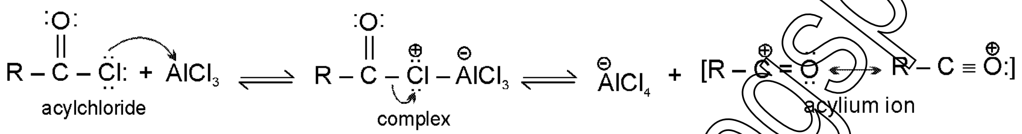
(iii) 

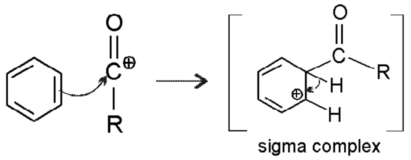
Acylation mechanism

Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.

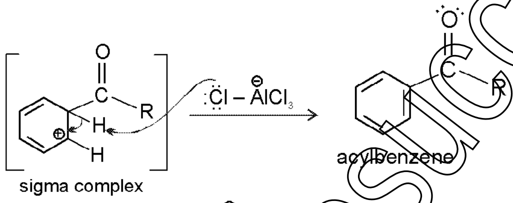
Step 1 : Formation of an acylium ion.

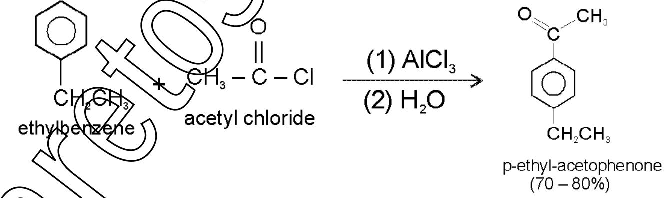

$$R-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{Cl}}: + AlCl_3 \rightleftharpoons R-\overset{\overset{:O:}{\|}}{C}-\overset{\oplus}{\underset{..}{Cl}}-\overset{\ominus}{Al}Cl_3 \rightleftharpoons \overset{\ominus}{Al}Cl_4 + [R-\overset{\oplus}{C}=\ddot{O} \longleftrightarrow R-C\equiv\overset{\oplus}{O}:]$$

Step 2 : electrophilic attack.

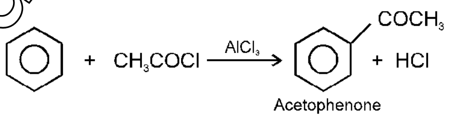


Step 3 : Loss of a proton. Complexation of the product.

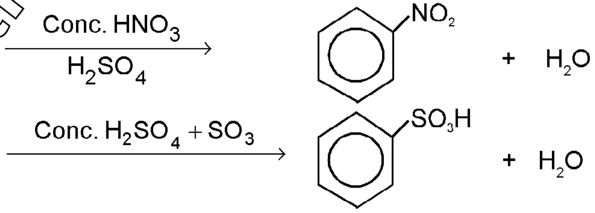


e.g. 

Note : Friedal - Crafts acylations are generally free from rearrangements and multiple substitution. They do not go on strongly deactivated rings.

e.g. 

Chemical Reactions of Benzene :



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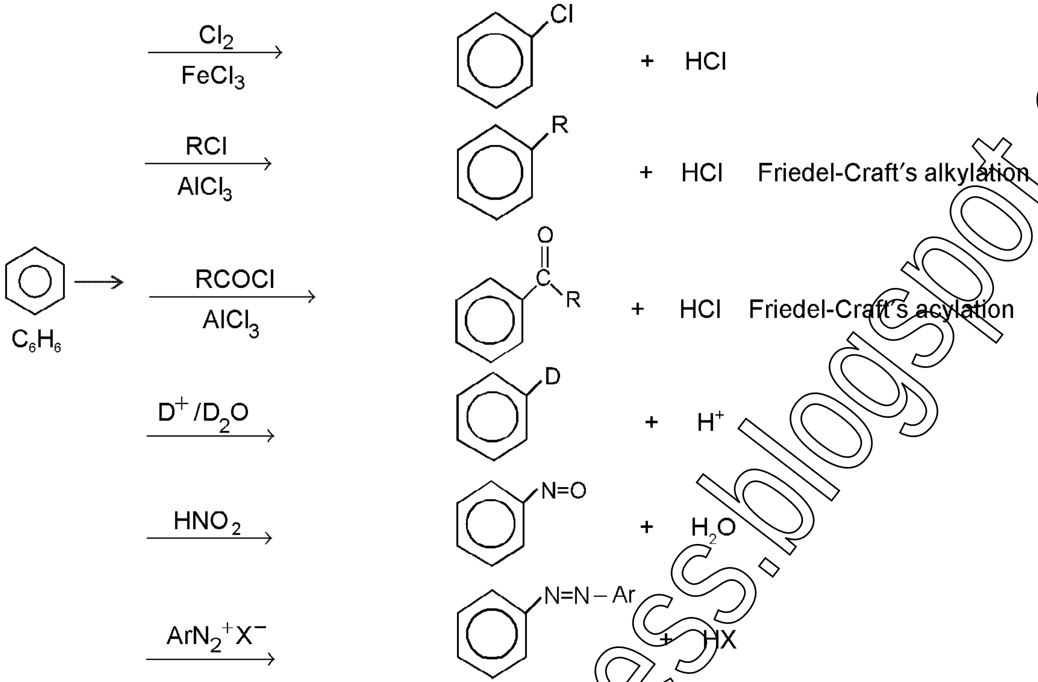
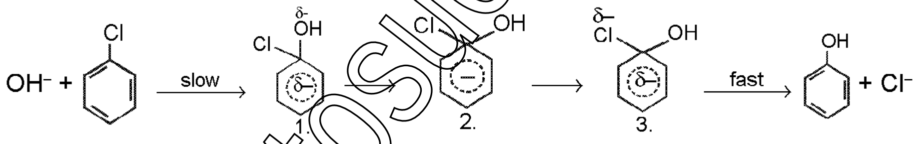


Nucleophilic Aromatic Substitution :

The reaction is second-order in which nucleophilic sbustitution occurs on benzene ring. It is generally accepted that the reaction proceeds via an intermediate σ-complex, the benzenonium carbanion (or the pentadienyl anion), e.g.,



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6. Chemical Reactions of Phenol

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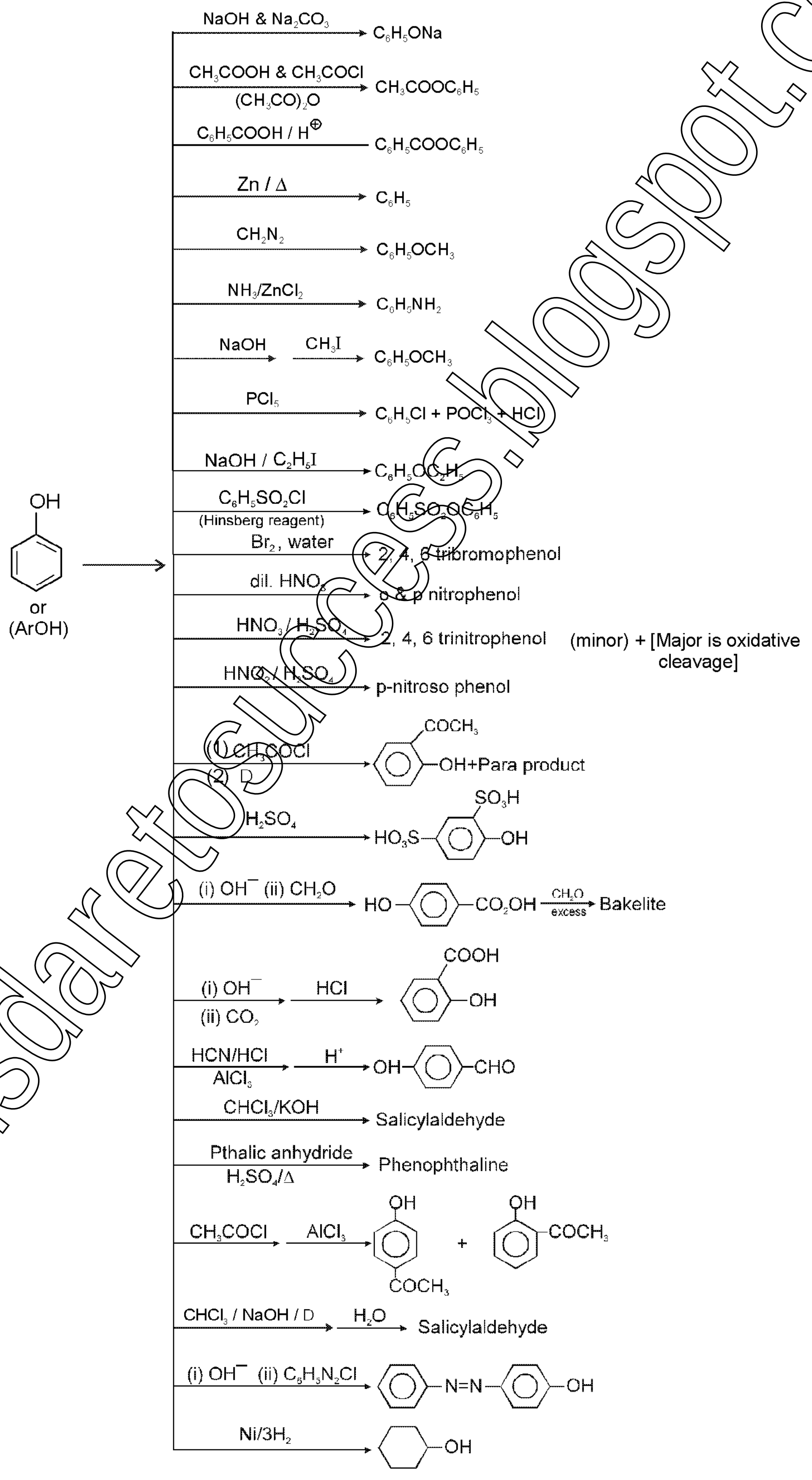
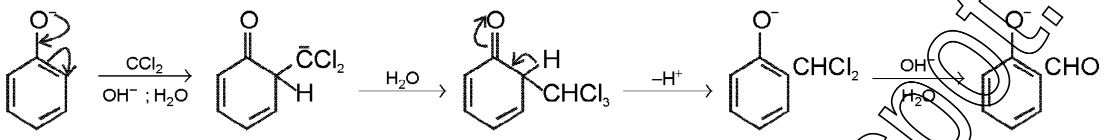


Reimer-Tiemann reaction :

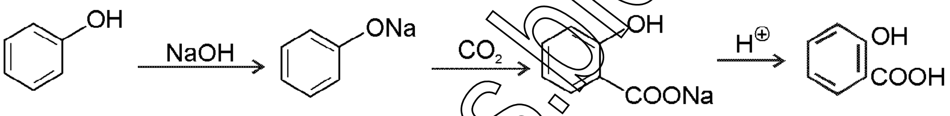
The reaction is conversion of phenol to salicylaldehyde. The mechanism of the Reimer-Tiemann reaction is believed to involve the formation of dichloromethylene.



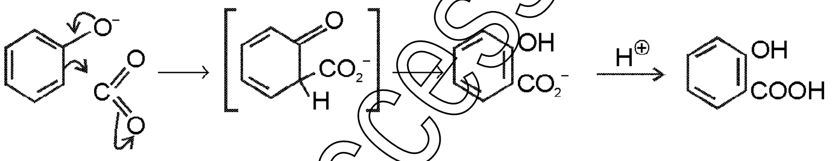
Kolbe Reaction :

It is the industrial method of preparation of salicylic acid from phenol.

General reaction :



Mechanism

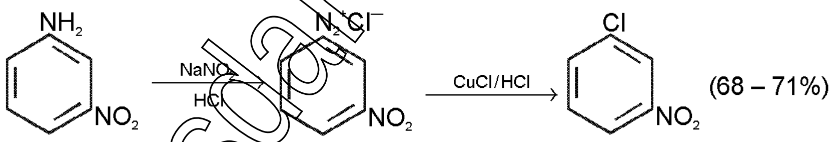


7. Chemical reactions of aniline

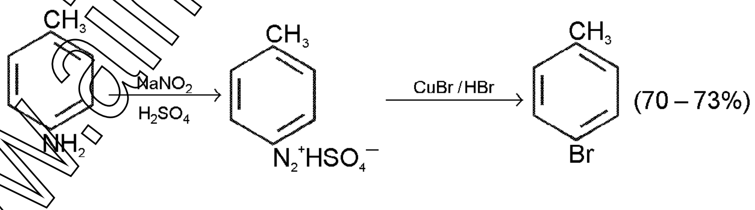
Sandmyer's Reaction :

When a diazonium salt solution is run into a solution of cuprous halide dissolved in the corresponding halogen acid, the diazo-group is replaced by a halogen atom.

m – Chloronitrobenzene



p – Bromotoluene



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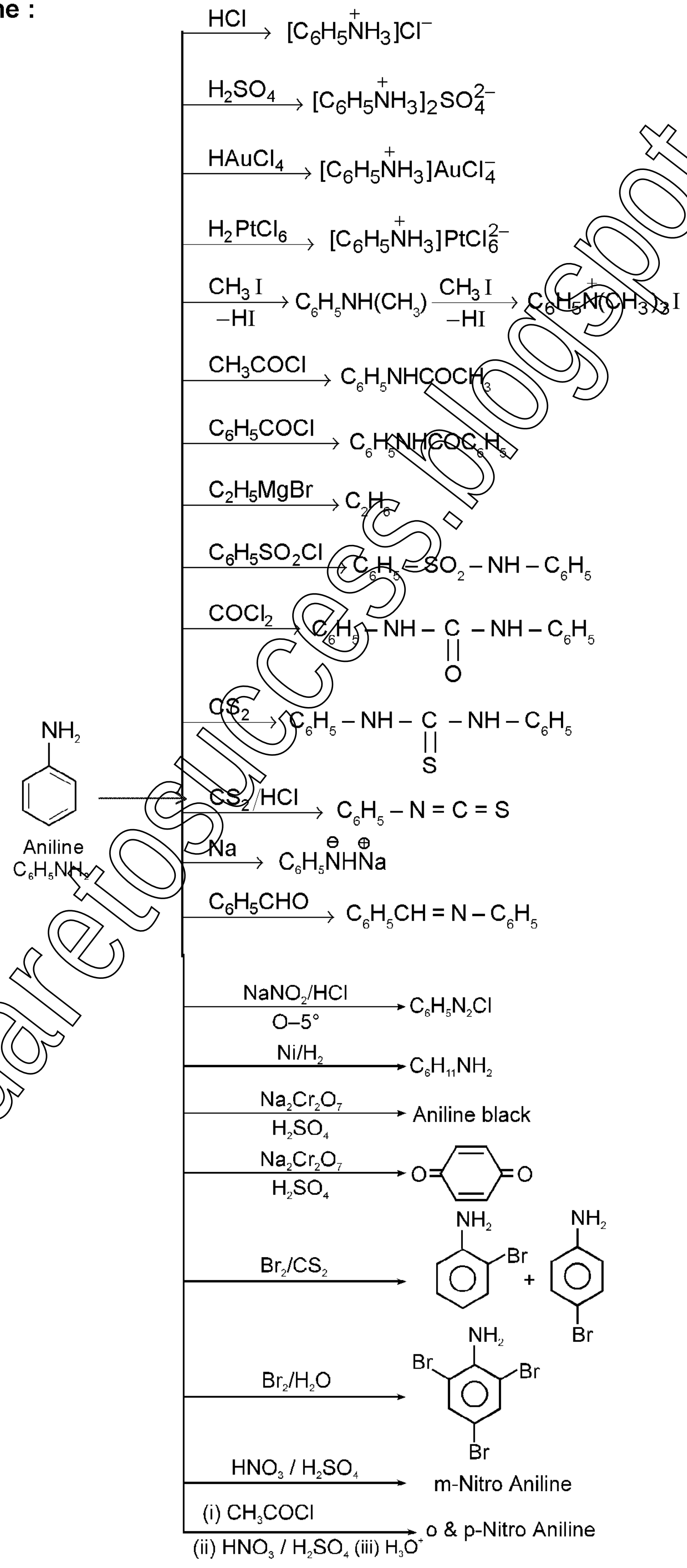
Chemical Reactions of Aniline :



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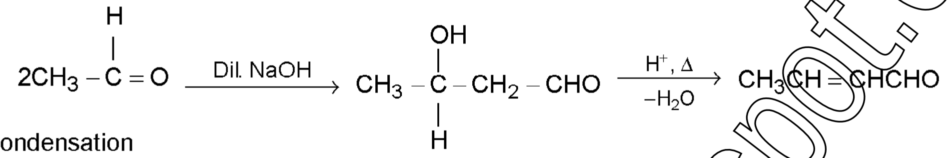
8. Aldehyde & ketone

Aldol condensation :

Carbonyl compounds having acidic α - H shows this reaction in presence of dil. NaOH or dil. acid.



$$2CH_3-\overset{H}{\overset{|}{C}}=O \xrightarrow{\text{Dil. NaOH}} CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-CHO \xrightarrow[-H_2O]{H^+,\ \Delta} CH_3CH=CHCHO$$

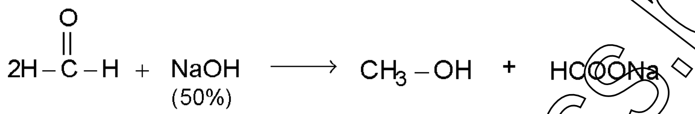
Crossed aldol condensation

(i) $CH_3CHO + HCHO \xrightarrow{\text{Dil. NaOH}} HOCH_2-CH_2-CHO \xrightarrow[\Delta]{H^+ / H_2O} CH_2=CH-CHO$

(ii) $CH_3COCH_3 + HCHO \xrightarrow{\text{Dil. NaOH}} CH_3CO-CH_2CH_2OH \xrightarrow[\Delta]{H^+ / H_2O} CH_3CO-CH=CH_2$

Cannizzaro reaction :

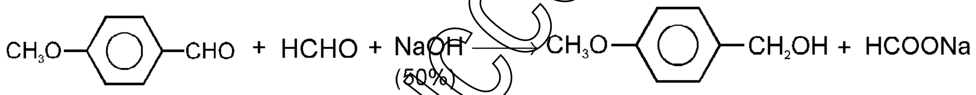
Carbonyl compounds not having α-H shows following disproportion reaction



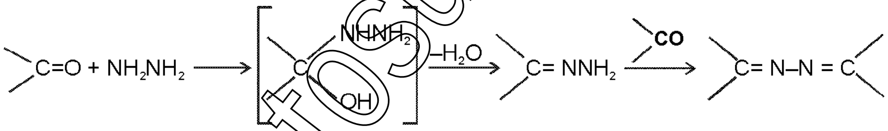
$$2H-\overset{O}{\overset{||}{C}}-H + \underset{(50\%)}{NaOH} \longrightarrow CH_3-OH + HCOONa$$

$$2C_6H_5CHO + \underset{(50\%)}{NaOH} \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Crossed Cannizzaro reaction :



Formation of hydrzones and azines



Amides formation :

$RCO_2H + CO(NH_2)_2 \longrightarrow RCONH_2 + CO_2 + NH_3$ (g. –v.g.)

$RCOCl + 2NH_3 \longrightarrow RCONH_2 + NH_4Cl$ (v.g.)

$(RCO)_2O + 2NH_3 \longrightarrow RCONH_2 + RCO_2NH_4$ (v.g.)

$R^1COOR^2 + NH_3 \longrightarrow R^1CONH_2 + R^2OH$ (g.)

Carbyl amine reaction

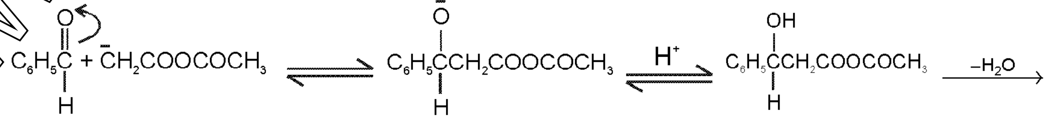
$RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

Perkin reaction :

When benzaldehyde (or any other aromatic aldehyde) is heated with the anhydride of an aliphatic acid (containing two α-hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β-arylacrylic acid ; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na} C_6H_5CH=CHCO_2H$$

$$CH_3COOCOCH_3 + CH_3CO_2^- \rightleftharpoons \bar{C}H_2COOCOCH_3 + CH_3CO_2H$$



$$C_6H_5\underset{H}{\underset{|}{\overset{O}{\overset{||}{C}}}} + \bar{C}H_2COOCOCH_3 \rightleftharpoons C_6H_5\underset{H}{\underset{|}{\overset{\bar{O}}{\overset{|}{C}}}}CH_2COOCOCH_3 \overset{H^+}{\rightleftharpoons} C_6H_5\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}CH_2COOCOCH_3 \xrightarrow{-H_2O}$$

$$C_6H_5CH=CHCOOCOCH_3 \xrightarrow{H_2O} C_6H_5CH=CHCO_2H + CH_3CO_2H$$

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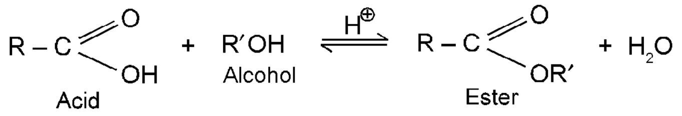
9. Ester formation

General reaction

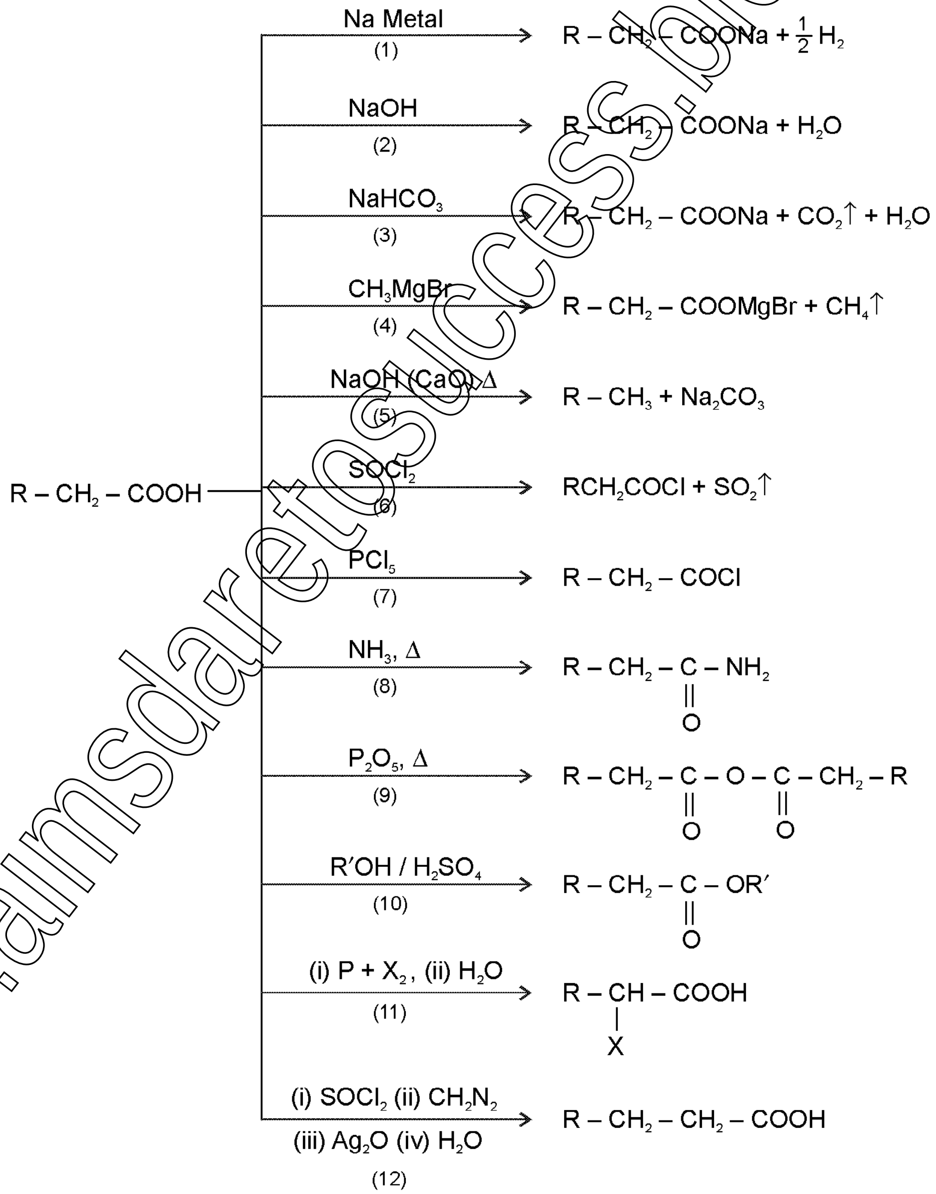


$$R-C(=O)OH + R'OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-C(=O)OR' + H_2O$$

Hydrolysis of ester $R^1CO_2H + R^2OH \xleftarrow{H_3O^+} R^1CO_2R^2 \xrightarrow{OH^-} R^1CO_2^- + R^2OH$

10. Carboxylic Acids

Chemical Reactions of acids



$R-CH_2-COOH \xrightarrow[(1)]{\text{Na Metal}} R-CH_2-COONa + \frac{1}{2}H_2$

$R-CH_2-COOH \xrightarrow[(2)]{NaOH} R-CH_2-COONa + H_2O$

$R-CH_2-COOH \xrightarrow[(3)]{NaHCO_3} R-CH_2-COONa + CO_2\uparrow + H_2O$

$R-CH_2-COOH \xrightarrow[(4)]{CH_3MgBr} R-CH_2-COOMgBr + CH_4\uparrow$

$R-CH_2-COOH \xrightarrow[(5)]{NaOH\,(CaO)\,\Delta} R-CH_3 + Na_2CO_3$

$R-CH_2-COOH \xrightarrow[(6)]{SOCl_2} RCH_2COCl + SO_2\uparrow$

$R-CH_2-COOH \xrightarrow[(7)]{PCl_5} R-CH_2-COCl$

$R-CH_2-COOH \xrightarrow[(8)]{NH_3,\ \Delta} R-CH_2-C(=O)-NH_2$

$R-CH_2-COOH \xrightarrow[(9)]{P_2O_5,\ \Delta} R-CH_2-C(=O)-O-C(=O)-CH_2-R$

$R-CH_2-COOH \xrightarrow[(10)]{R'OH\,/\,H_2SO_4} R-CH_2-C(=O)-OR'$

$R-CH_2-COOH \xrightarrow[(11)]{(i)\ P + X_2,\ (ii)\ H_2O} R-CH(X)-COOH$

$R-CH_2-COOH \xrightarrow[(iii)\ Ag_2O\ (iv)\ H_2O]{(i)\ SOCl_2\ (ii)\ CH_2N_2} R-CH_2-CH_2-COOH$ (12)

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Identification of Functional Groups by Laboratory Tests (POC)

Table :

Functional Groups	Reagent	Observation	Reaction	Remarks
$C = C$ / $C \equiv C$	[Bayer's reagent] alk. dil. cold $KMnO_4$	Pink colour Disappears	$CH_2 = CH_2 + H_2O + O \xrightarrow{\text{alk.}KMnO_4} \underset{OH}{\underset{\mid}{CH_2}}-\underset{OH}{\underset{\mid}{CH_2}}$	Hydroxylation
	Br_2 / H_2O	Red colour decolourises	$Br_2 + CH_2 = CH_2 \longrightarrow$ white ppt	Bromination
$R-C \equiv CH$	(a) Cuprous chloride + NH_4OH	Red ppt.	$R-C \equiv CH + CuCl \xrightarrow{NH_4OH} R-C \equiv CCu\downarrow$ (red)	
	(b) $AgNO_3 + NH_4OH$	White ppt.	$R-C \equiv CH + Ag^+ \longrightarrow R-C \equiv CAg\downarrow$ (white)	
ROH 3° 2° 1°	Lucas Reagent [Conc. HCl + anhyd. $ZnCl_2$]	(3)° Cloudiness appears immidiately (2°) Cloudiness appears within 5 min. (1°) Cloudiness appear after 30 min.	$R-OH + HCl \xrightarrow{\text{anhydrous}ZnCl_2} \underbrace{R-Cl + H_2O}_{\text{cloudiness}}$	Lucas Test I. ter.alcohol II. sec. alcohol III. pri.alcohol

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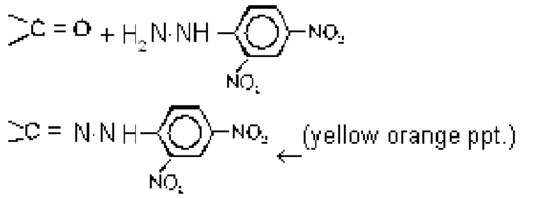
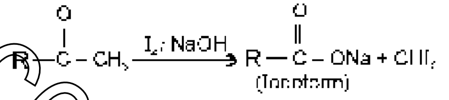
Functional Groups	Reagent	Observation	Reaction	Remarks
Ar – OH Enols	$FeCl_3$ (Neutral)	Coloured ppt. (violet, blue, green buff)	$6\,C_6H_5OH + FeCl_3 \longrightarrow [Fe(PhO)_6]^{-3}$	Test of enols / phenols
$>C=O$	2, 4-Dinitrophenyl hydrazine (2, 4-DNP) solution	Yellow orange ppt.	 (yellow orange ppt.)	DNP-test
R – CHO	Fehling solution A & B	Red ppt.	RCHO + Cu^{+2} Fehling sol^n. RCOOH + Cu_2O Red $\leftarrow$ + $2H_2O$	Fehling's test
	Tollen's reagent	Black ppt. or silver mirror	RCHO + Ag^+ $\downarrow$ RCOOH + 2Ag (Silver mirror)	Tollen's test
	Schift's Reagent *	Pink colour resume		
$R-COCH_3$ or $ArCOCH_3$ or CH_3CHO	I_2 / NaOH	Yellow ppt of CHI_3 (iodoform)	 $R-\overset{O}{\overset{\parallel}{C}}-CH_3 \xrightarrow{I_2/NaOH} R-\overset{O}{\overset{\parallel}{C}}-ONa + \underset{(Iodoform)}{CHI_3}$	Iodoform reaction
$R-\overset{O}{\overset{\parallel}{C}}-OH$	Blue litmus	Litmus change to red.		Litmus test.
	Conc. $NaHCO_3$ solution	Effervescence evolve.	R – COOH + $NaHCO_3 \longrightarrow$ R COO Na + $H_2O + CO_2 \uparrow$	Sodium bicarbonate test

★ Schift's reagent : p-Rosiniline hydrochloride saturated with SO_2 so it is colourless. The pink colour is resumed by RCHO.

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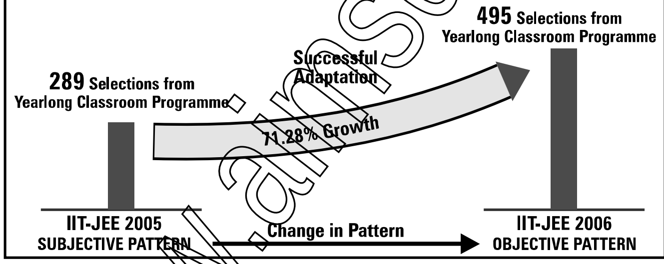

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