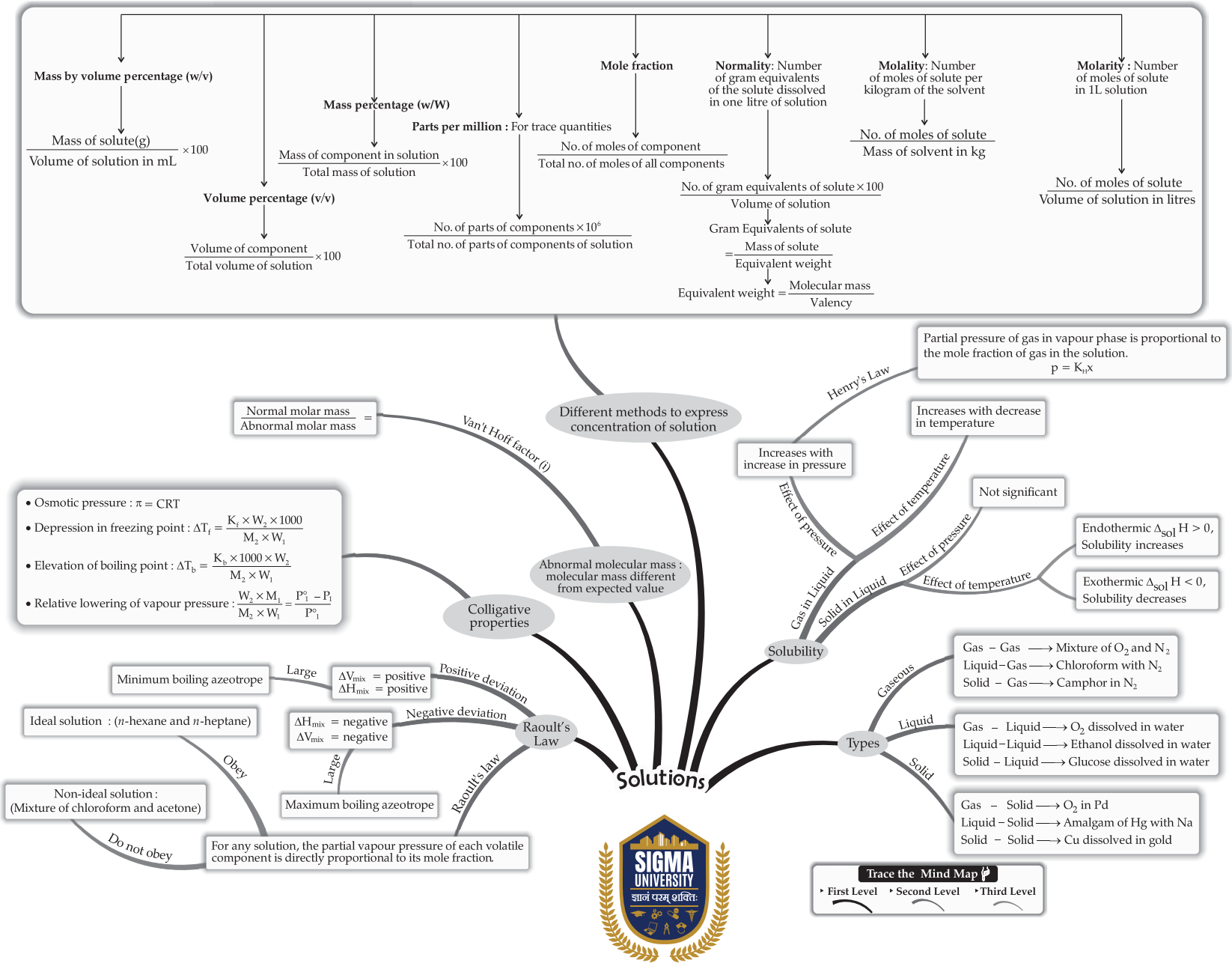
Solutions
Different methods to express concentration of solution
Mass by volume percentage (w/v)
Mass of solute(g) / Volume of solution in mL × 100
Mass percentage (w/W)
Mass of component in solution / Total mass of solution × 100
Volume percentage (v/v)
Volume of component / Total volume of solution × 100
Parts per million : For trace quantities
No. of parts of components × 10^6 / Total no. of parts of components of solution
Mole fraction
No. of moles of component / Total no. of moles of all components
Normality : Number of gram equivalents of the solute dissolved in one litre of solution
No. of gram equivalents of solute × 100 / Volume of solution
Gram Equivalents of solute = Mass of solute / Equivalent weight
Equivalent weight = Molecular mass / Valency
Molality : Number of moles of solute per kilogram of the solvent
No. of moles of solute / Mass of solvent in kg
Molarity : Number of moles of solute in 1L solution
No. of moles of solute / Volume of solution in litres
Colligative properties
• Osmotic pressure : π = CRT
• Depression in freezing point : ΔT_f = K_f × W_2 × 1000 / M_2 × W_1
• Elevation of boiling point : ΔT_b = K_b × 1000 × W_2 / M_2 × W_1
• Relative lowering of vapour pressure : W_2 × M_1 / M_2 × W_1 = P°_1 − P_1 / P°_1
Abnormal molecular mass : molecular mass different from expected value
Normal molar mass / Abnormal molar mass =
Van't Hoff factor (i)
Raoult's Law
For any solution, the partial vapour pressure of each volatile component is directly proportional to its mole fraction.
Ideal solution : (n-hexane and n-heptane)
Obey
Non-ideal solution : (Mixture of chloroform and acetone)
Do not obey
Raoult's law
Positive deviation
ΔV_mix = positive
ΔH_mix = positive
Large
Minimum boiling azeotrope
Negative deviation
ΔH_mix = negative
ΔV_mix = negative
Large
Maximum boiling azeotrope
Solubility
Henry's Law
Partial pressure of gas in vapour phase is proportional to the mole fraction of gas in the solution.
p = K_H x
Gas in Liquid
Increases with increase in pressure
Effect of pressure
Effect of temperature
Increases with decrease in temperature
Solid in Liquid
Effect of pressure
Not significant
Effect of temperature
Endothermic Δ_sol H > 0, Solubility increases
Exothermic Δ_sol H < 0, Solubility decreases
Types
Gaseous
Gas – Gas ⟶ Mixture of O_2 and N_2
Liquid – Gas ⟶ Chloroform with N_2
Solid – Gas ⟶ Camphor in N_2
Liquid
Gas – Liquid ⟶ O_2 dissolved in water
Liquid – Liquid ⟶ Ethanol dissolved in water
Solid – Liquid ⟶ Glucose dissolved in water
Solid
Gas – Solid ⟶ O_2 in Pd
Liquid – Solid ⟶ Amalgam of Hg with Na
Solid – Solid ⟶ Cu dissolved in gold
Trace the Mind Map
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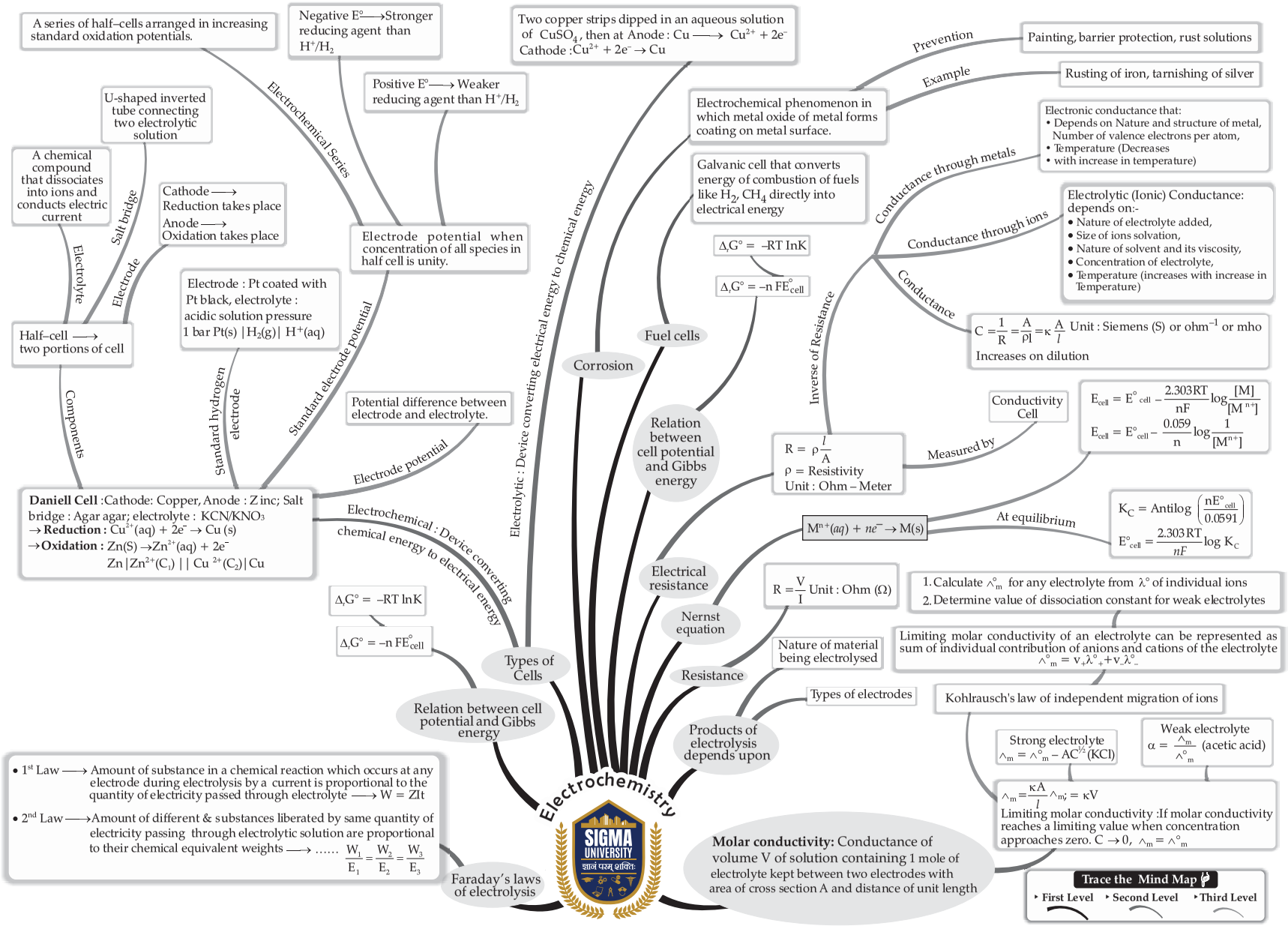
Electrochemistry
Electrochemical Series
A series of half–cells arranged in increasing standard oxidation potentials.
Negative E°⟶Stronger reducing agent than H⁺/H₂
Positive E°⟶ Weaker reducing agent than H⁺/H₂
Electrode potential when concentration of all species in half cell is unity.
Standard electrode potential
Standard hydrogen electrode
Electrode : Pt coated with Pt black, electrolyte : acidic solution pressure 1 bar Pt(s) |H₂(g)| H⁺(aq)
Components
Half–cell ⟶ two portions of cell
Electrolyte
Salt bridge
Electrode
A chemical compound that dissociates into ions and conducts electric current
U-shaped inverted tube connecting two electrolytic solution
Cathode ⟶ Reduction takes place
Anode ⟶ Oxidation takes place
Daniell Cell :Cathode: Copper, Anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO₃
→Reduction : Cu²⁺(aq) + 2e⁻ → Cu (s)
→Oxidation : Zn(S) →Zn²⁺(aq) + 2e⁻
Zn |Zn²⁺(C₁) | | Cu ²⁺(C₂)|Cu
Electrode potential
Potential difference between electrode and electrolyte.
Electrochemical : Device converting chemical energy to electrical energy
Electrolytic : Device converting electrical energy to chemical energy
Two copper strips dipped in an aqueous solution of CuSO₄, then at Anode : Cu ⟶ Cu²⁺ + 2e⁻
Cathode :Cu²⁺ + 2e⁻ → Cu
Corrosion
Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.
Prevention
Painting, barrier protection, rust solutions
Example
Rusting of iron, tarnishing of silver
Fuel cells
Galvanic cell that converts energy of combustion of fuels like H₂, CH₄ directly into electrical energy
Relation between cell potential and Gibbs energy
ΔrG° = –RT InK
ΔrG° = –n FE°cell
Types of Cells
ΔrG° = –RT lnK
ΔrG° = –n FE°cell
Relation between cell potential and Gibbs energy
Inverse of Resistance
Conductance through metals
Electronic conductance that:
• Depends on Nature and structure of metal, Number of valence electrons per atom,
• Temperature (Decreases
• with increase in temperature)
Conductance through ions
Electrolytic (Ionic) Conductance: depends on:-
• Nature of electrolyte added,
• Size of ions solvation,
• Nature of solvent and its viscosity,
• Concentration of electrolyte,
• Temperature (increases with increase in Temperature)
Conductance
C = 1/R = A/ρl = κ A/l Unit : Siemens (S) or ohm⁻¹ or mho
Increases on dilution
Conductivity Cell
Measured by
R = ρ l/A
ρ = Resistivity
Unit : Ohm – Meter
Electrical resistance
Nernst equation
Resistance
R = V/I Unit : Ohm (Ω)
Nature of material being electrolysed
Types of electrodes
Products of electrolysis depends upon
Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.
Mⁿ⁺(aq) + ne⁻ → M(s)
At equilibrium
E_cell = E°_cell – 2.303RT/nF log [M]/[Mⁿ⁺]
E_cell = E°_cell – 0.059/n log 1/[Mⁿ⁺]
K_C = Antilog (nE°_cell/0.0591)
E°_cell = 2.303RT/nF log K_C
1. Calculate ∧°m for any electrolyte from λ° of individual ions
2. Determine value of dissociation constant for weak electrolytes
Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte
∧°m = ν₊λ°₊+ν₋λ°₋
Kohlrausch's law of independent migration of ions
Strong electrolyte ∧m = ∧°m – AC^½(KCl)
Weak electrolyte α = ∧m/∧°m (acetic acid)
∧m = κA/l ∧m; = κV
Limiting molar conductivity :If molar conductivity reaches a limiting value when concentration approaches zero. C → 0, ∧m = ∧°m
Molar conductivity: Conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length
Faraday's laws of electrolysis
• 1st Law ⟶ Amount of substance in a chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte ⟶ W = ZIt
• 2nd Law ⟶Amount of different & substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weights ⟶ ..... W1/E1 = W2/E2 = W3/E3
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Chemical Kinetics

Order	Integrated Rate Law	Straight Plot	Unit (k)
0	$kt = [R]_0 - [R]$	[R] vs t	mol L^{-1} s^{-1}
1	$kt = \ln \{[R]_0/[R]\}$	ln[R] vs t	s^{-1}

Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Time in which the concentration of a reactant is reduced to one half of its initial concentration.

First Order: $t_{1/2} = \frac{0.693}{k}$

Zero Order: $t_{1/2} = \frac{[R]_0}{2k}$

Integrated Rate Equation

Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Half-life of a Reaction

Not truly of first order but under certain conditions behave as first order reaction. In such reaction, one reactants is in excess.
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

Molecularity of a Reaction

Pseudo First Order Reaction

Activation Energy, E_a : Energy required to form an intermediate called activated complex (C)
E_a = Threshold energy - Average Kinetic energy of reacting molecules

Arrhenius Equation

$$k = Ae^{-Ea/RT}$$
$$\log k = \log A - \frac{E_a}{2.303RT}$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Rate of appearance of P $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\triangle[P]}{\triangle t}$

Rate of disappearance of R $= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = \frac{-\triangle[R]}{\triangle t}$

$R \rightarrow P$

Appearance of products or disappearance of reactants over a long time interval.

$r_{av} = \frac{\Delta[P]}{\Delta t}$ = slope

$r_{av} = \frac{-\Delta[R]}{\Delta t}$ = –slope

Average Rate

Change in concentration of reactants or products in unit time; Unit : mol L^{-1} s^{-1} or atm s^{-1}

Factors Influencing rate of reaction

Concentration : Higher the concentration of reactants, faster is the rate of reaction.
Temperature : Increases with increase in temperature. Becomes almost double with 10°C rise.
Catalyst : Increases with a catalyst.
Surface Area : Greater is the surface area, faster is the rate of reaction.
Activation Energy : Lower the activation energy, faster is the reaction.

Instantaneous Rate

Rate of change in concentration of reactant/product at a particular time.

$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$

Rate Law

Expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation.

$aA + bB \rightarrow cC + dD$

$\text{Rate} = k[A]^a[B]^b = \frac{d[R]}{dt}$

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

Rate Constant: Rate of a reaction when concentration of each of the reactant in unity.

Order	Unit
0	mol $L^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}L\ s^{-1}$

Rate of Chemical Reaction

Sum of powers of concentration of the reactants in the rate law.

Order of a Reaction

Collision Theory : Rate of reaction depends on the collision frequency and effective collisions.

Effective Collision

Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.

Collision Frequency

E_a and proper orientation of the molecules determine the criteria for an effective collision.

$\text{Rate} = PZ_{AB}e^{-Ea/RT}$
P is Steric or Probability factor

Number of collisions per unit volume of reaction mixture
$\text{Rate} = Z_{AB}e^{-Ea/RT}$

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d– and f– Block Elements

- **Position :** Between *s*- and *p*–blocks.
- **Electronic configuration :** $(n-1)d^{1-10}ns^{1-2}$
- **Physical properties :** Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization.
- Decrease in radius with increasing atomic number. 'Lanthanoid contraction is due to filling of 4f before 5d orbitals, hence 2^{nd}, 3^{rd} d-series exhibit similar radii. Also due to imperfect shielding of one e^- by another in the same set of orbitals in same set of orbitals.'
- **Ionisation enthalpies :** Increases from left to right.
- **Oxidation states :** Variable; higher oxidation number stable.
- Trends in M^{2+}/M E° : E° for Mn, Ni and Zn are more negative than expected.
- Trends in M^{3+}/M^{2+} E° : Variable.
- **Chemical reactivity and E° values :** Variable; Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents.
- **Magnetic properties :** Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- **Formation of coloured ions :** Form coloured compounds due to d-d transitions.
- **Formation of complex compounds :** Form a large number of complex compounds.
- **Catalytic properties :** Due to variable oxidation states and ability to form complexes.
- **Forms interstitial compounds :** Non-stoichiometric and are neither ionic nor covalent.

d–Block transition elements groups 3–12

Uses

- Helps in production of iron and steels.
- TiO in pigment industry.
- MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes useful in the polymerization of alkynes and other organic compounds such as benzene.
- AgBr in photographic industry.

f– Block Transition Elements

Actinoids

Lanthanoid contraction is progressive decrease in atomic/ionic radii from La^{3+} to Lu^{3+}

Lanthanoids

- Electronic configuration: $[Rn]5f^{1-14}\ 6d^{0-1}\ 7s^2$
- Ionic sizes : Gradual decrease along the series.
- Oxidation states : Most common is +3. They show oxidation number of +4, +5, +6 and +7.
- **General characteristics :**
  - –Silvery in appearance.
  - –Display variety of structures.
  - –Highly reactive metals.
  - –Irregularities in metallic radii, greater than in lanthanoids.
  - –Magnetic properties more complex than lanthanoids.

- Electronic configuration : $4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Atomic and ionic sizes : Decrease from La to Lu
- Oxidation states : Most common is +3. Some elements exhibit +2 and +4.
- **General characteristics :**
  - Silvery white soft metals and tarnish rapidly in air.
  - Hardness increases with increasing atomic number.
  - Metallic structure and good conductors of heat and electricity.
- Variable density.
- Trivalent lanthanoid ions are coloured.
- Ionisation Enthalpies : Low third ionisation enthalpies.
- Good reducing agents.

Oxides and oxoanions of metals

- Potassium dichromate $K_2Cr_2O_7$

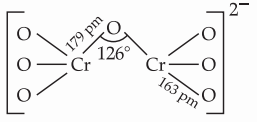
Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Properties : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Oxidises iodides to iodine, H_2S to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



- Potassium permanganate $KMnO_4$

Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

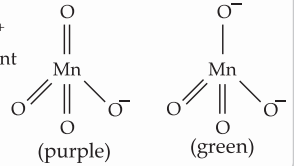
$3\,MnO_4^{2-} + 4H^+ \rightarrow 2\,MnO_4^- + MnO_2 + 2H_2O$

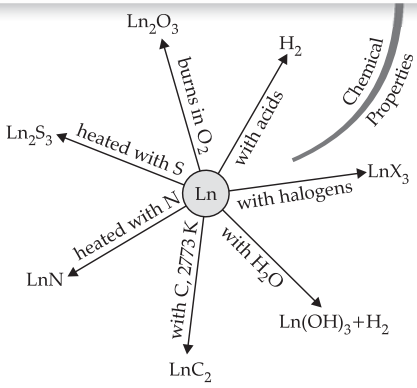
$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2\,MnO_4^- + 10\,SO_4^{2-} + 16H^+$

Properties : Intense colour, weak temperature dependent paramagnetism

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Oxidizes I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-





Trace the Mind Map

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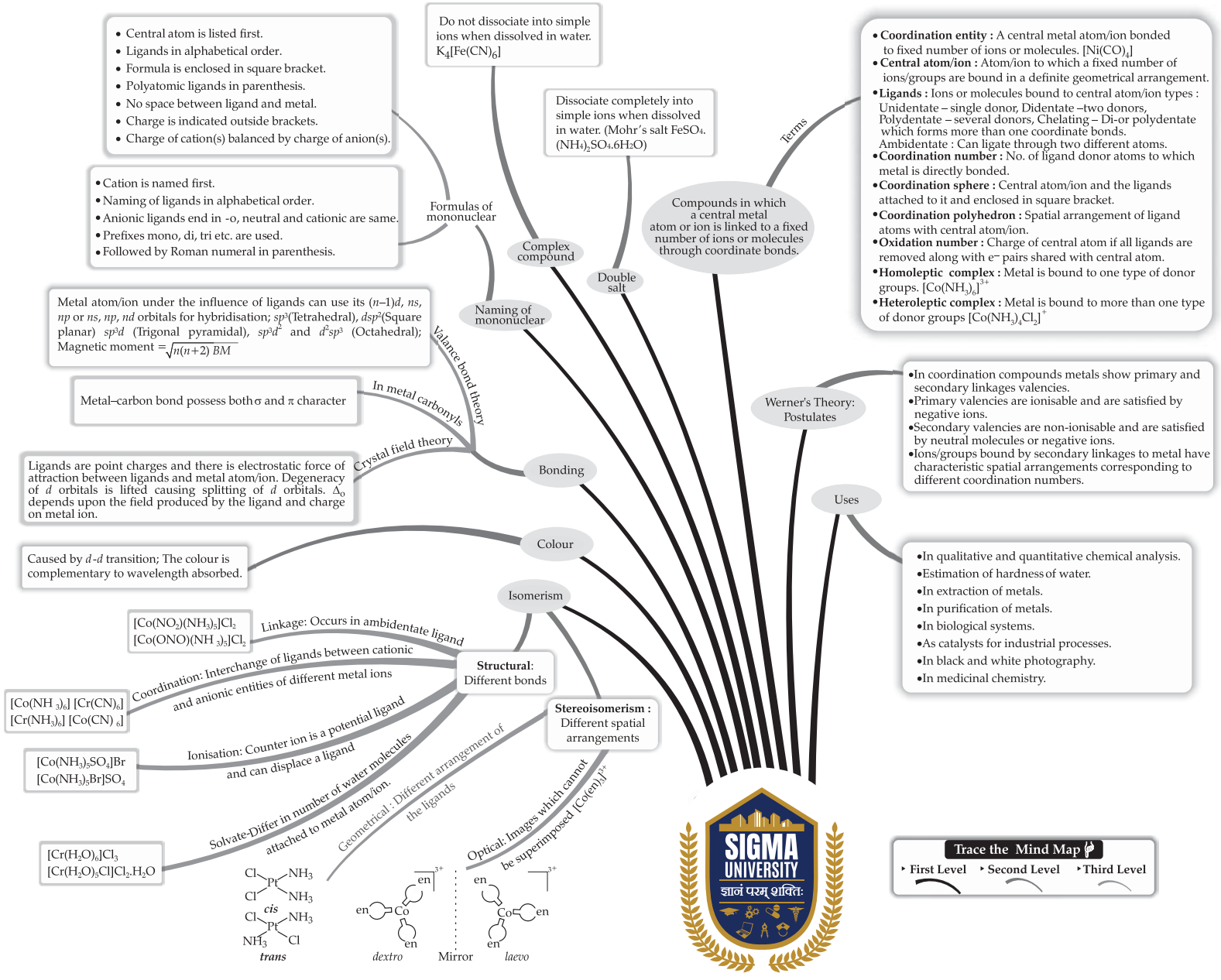
Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.
Terms
• Coordination entity : A central metal atom/ion bonded to fixed number of ions or molecules. [Ni(CO)4]
• Central atom/ion : Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
• Ligands : Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate –two donors, Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
• Coordination number : No. of ligand donor atoms to which metal is directly bonded.
• Coordination sphere : Central atom/ion and the ligands attached to it and enclosed in square bracket.
• Coordination polyhedron : Spatial arrangement of ligand atoms with central atom/ion.
• Oxidation number : Charge of central atom if all ligands are removed along with e⁻ pairs shared with central atom.
• Homoleptic complex : Metal is bound to one type of donor groups. [Co(NH3)6]3+
• Heteroleptic complex : Metal is bound to more than one type of donor groups [Co(NH3)4Cl2]+
Complex compound
Do not dissociate into simple ions when dissolved in water. K4[Fe(CN)6]
Double salt
Dissociate completely into simple ions when dissolved in water. (Mohr's salt FeSO4.(NH4)2SO4.6H2O)
Naming of mononuclear
Formulas of mononuclear
• Central atom is listed first.
• Ligands in alphabetical order.
• Formula is enclosed in square bracket.
• Polyatomic ligands in parenthesis.
• No space between ligand and metal.
• Charge is indicated outside brackets.
• Charge of cation(s) balanced by charge of anion(s).
• Cation is named first.
• Naming of ligands in alphabetical order.
• Anionic ligands end in -o, neutral and cationic are same.
• Prefixes mono, di, tri etc. are used.
• Followed by Roman numeral in parenthesis.
Bonding
Valance bond theory
Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp3(Tetrahedral), dsp2(Square planar) sp3d (Trigonal pyramidal), sp3d2 and d2sp3 (Octahedral); Magnetic moment = √n(n+2) BM
In metal carbonyls
Metal–carbon bond possess both σ and π character
Crystal field theory
Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lifted causing splitting of d orbitals. Δo depends upon the field produced by the ligand and charge on metal ion.
Colour
Caused by d-d transition; The colour is complementary to wavelength absorbed.
Isomerism
Structural: Different bonds
[Co(NO2)(NH3)5]Cl2
[Co(ONO)(NH3)5]Cl2
Linkage: Occurs in ambidentate ligand
Coordination: Interchange of ligands between cationic and anionic entities of different metal ions
[Co(NH3)6] [Cr(CN)6]
[Cr(NH3)6] [Co(CN)6]
Ionisation: Counter ion is a potential ligand and can displace a ligand
[Co(NH3)5SO4]Br
[Co(NH3)5Br]SO4
Solvate-Differ in number of water molecules attached to metal atom/ion.
[Cr(H2O)6]Cl3
[Cr(H2O)5Cl]Cl2.H2O
Stereoisomerism : Different spatial arrangements
Geometrical : Different arrangement of the ligands
cis
trans
Optical: Images which cannot be superimposed [Co(en)3]3+
dextro
Mirror
laevo
Werner's Theory: Postulates
•In coordination compounds metals show primary and secondary linkages valencies.
•Primary valencies are ionisable and are satisfied by negative ions.
•Secondary valencies are non-ionisable and are satisfied by neutral molecules or negative ions.
•Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.
Uses
•In qualitative and quantitative chemical analysis.
•Estimation of hardness of water.
•In extraction of metals.
•In purification of metals.
•In biological systems.
•As catalysts for industrial processes.
•In black and white photography.
•In medicinal chemistry.
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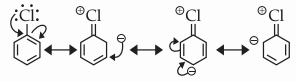
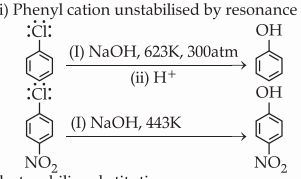
Haloalkanes and Haloarenes

Haloarenes

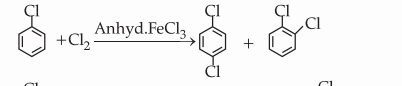
- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect

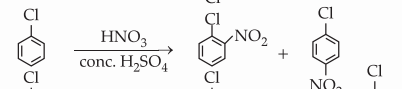


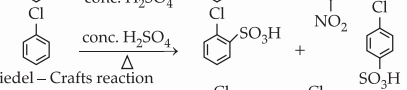
    - (ii) Hybridisation of C in C-X bond :
      Haloalkane –sp^3; Haloarene –sp^2
    - (iii) Phenyl cation unstabilised by resonance



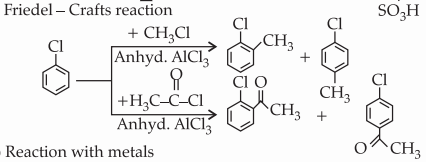
  - (b) Electrophilic substitution







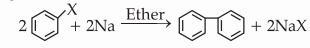
Friedel – Crafts reaction



  - (c) Reaction with metals

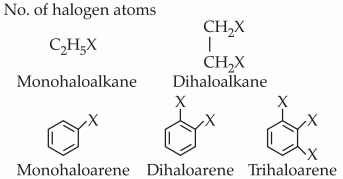
Wurtz – Fitting reaction

Fittig reaction

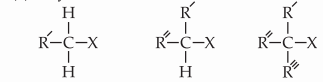


Classification

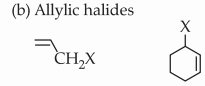
- No. of halogen atoms



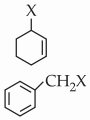
- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides



  - (b) Allylic halides



  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides
  - (b) Aryl halides

- Nomenclature
  Common name : Alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.
  IUPAC name : Numerals are used.
- Nature of C –X bond
  : Carbon –halogen bond is polarised.

Haloalkanes

=>Preparation

- From alcohol :

- From hydrocarbons :
  - (a) By free radical halogenation

  - (b) By electrophilic substitution

  - (c) Sandmeyer's reaction

  - (d) From alkenes

- Halogen exchange :
  R–X + NaI → R – I + NaX

=>Properties

- Physical : Colourless, volatile, sweet smell.
  Lower members are gases at room temperature while higher are solids.
  B.P : RI > RBr > RCl > RF.
  M.P : Para isomers have high m.p. than ortho and meta – isomers.
  Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.
  Solubility : Very slightly soluble in water.
- Chemical :
  - (a) Nucleophilic substitution

  - (b) Elimination reaction

  B = Base; X = Leaving group

  - (c) Reaction with metals
    $CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$
    Wurtz reaction :
    $2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$

Polyhalogen compounds

- Manufacture of refrigerants and propellants.
- Cleaning fluid.

Carbon tetrachloride

- Solvent for fats, alkaloids, I etc.
- Production of freon.

Chloroform

Antiseptic — Iodoform

For aerosol propellants, refrigeration and air conditioning purposes.

Freons

- Paint remover.
- Propellant in aerosols.
- Metal cleaning and finishing solvent.

Dichloromethane

As insecticide — DDT

S_N2 Stereochemical inversion

(a) Dextro (+/d)
(b) Laevo (–/l)

Racemisation S_N1

- Chiral : Objects which are non-superimposable.
- Achiral : Objects which are superimposable.

Trace the Mind Map
First Level · Second Level · Third Level

Alcohols, Phenols And Ethers

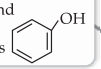
Classification

Alcohols

(i) Containing C_{sp^3} – OH bond

$-CH_2OH$ (1°) $>CHOH$ (2°) $>COH$ (3°)

(ii) Containing C_{sp^2} -OH bond

Vinylic alcohol : $CH_2 = CH - OH$ Phenols 

Mono, Di, Tri, or polyhydric :

Ethers

(i) Simple/symmetrical : Alkyl or aryl attached to oxygen atom same.

(ii) Mixed/unsymmetrical : Two groups are different.

Nomenclature

Alcohols : Common name : Alkyl group + ol; IUPAC name : substituting 'e' of alkane with suffix 'ol'

Phenols : Common name : Terms ortho, meta and para are used. IUPAC name : Dihydroxy derivatives as 1,2–, 1,3– and 1,4 –benzenediol

Ethers : Common name : Alkyl/aryl groups in alphabetical order followed by ether. IUPAC name : In alkyl /aryl group 'e' replaced by oxy followed by parent hydrocarbon.

Structures of functional groups

- Oxygen of –OH group is attached to C by a σ bond formed by the overlap of sp^3 orbital of C with a sp^3 orbital of oxygen.
- In ethers, tetrahedral arrangement for four electron pairs.

Properties

Alcohols

(i) Physical : •Boiling point increases with increase in the number of C atoms.
•Solubility decreases with increase in size of alky/aryl groups.

(ii) Chemical : $2\text{–R–O–H} + 2\text{Na} \longrightarrow 2\text{R–O–Na} + H_2$;Acidity – primary > secondary > tertiary

$Ar/R\text{–O–H} + R' \text{–COOH} \overset{H^+}{\rightleftharpoons} Ar/R\text{-COOR'} + H_2O$; $ROH + HX \longrightarrow R\text{–X} + H_2O$

$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$; $RCH_2OH \xrightarrow{\text{Oxidation}} R\text{-}\overset{H}{\underset{OH}{C}}=O \longrightarrow R\text{-}\overset{OH}{\underset{OH}{C}}=O$

Phenol → Dil. HNO_3 → 2-Nitrophenol + 4-Nitrophenol

Phenol → Conc. HNO_3 → 2,4,6-Trinitrophenol

Phenol → Br_2 in CS_2, 273K → 4-Bromophenol + 2-Bromophenol

Phenol → $3Br_2$ → 2,4,6-Tribromophenol

Phenol → Zn → Benzene + ZnO

Phenol → $Na_2Cr_2O_7$, H_2SO_4 → 1,4-Benzoquinone

Kolbe's reaction : Phenol → NaOH → Sodium phenoxide → (i) CO_2 (ii) H^+ → Salicylic acid

Reimer Tiemann reaction : Phenol → $CHCl_3$, aqNaOH → Salicylaldehyde → NaOH → Sodium salicylaldehyde → H^+ → Salicylaldehyde

Preparation

Alcohols

1. From alkenes :- (i) By acid catalysed hydration

$>C=C<+H_2O \overset{H^+}{\rightleftharpoons} >C-C<$ (H, OH)

(ii) By hydroboration – oxidation

$CH_3\text{–}CH=CH_2 + (H\text{–}BH_2)_2 \longrightarrow CH_3\text{–}\underset{H}{CH}\text{–}\underset{BH_2}{CH_2}$; $CH_3\text{–}CH=CH_2 \longrightarrow (CH_3\text{–}CH_2\text{–}CH_2)_3B$

$3CH_3\text{–}CH_2\text{–}CH_2\text{–}OH + B(OH)_3 \xleftarrow[3H_2O_2,OH]{H_2O} CH_3\text{–}CH_2\text{–}CH_2)_3BH\ (CH_3\text{–}CH=CH_2)$

2. From carbonyl compounds :

(i) By reduction of aldehydes and ketones

$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$, $RCOR' \xrightarrow{NaBH_4} R\text{–}\underset{OH}{CH}\text{–}R'$

(ii) By reduction of carboxylic acids and esters

$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{catalyst}]{H_2} RCH_2OH + R'OH$

3. From Grignard reagent

$>C=O + R\text{–}MgX \longrightarrow \left[>\underset{R}{C}\text{–}OMg\text{–}X\right] \xrightarrow{H_2O} >\underset{R}{C}\text{–}OH + Mg(OH)X$

Phenols

1. From haloarenes

Chlorobenzene + NaOH → (623K, 300atm) → Sodium phenoxide → HCl → Phenol

2. From benzene sulphonic acid

Benzenesulphonic acid → Oleum → (i) NaOH (ii) H^+ → Phenol

3. From diazonium salts

Aniline → $NaNO_2$, HCl → Benzenediazonium chloride → H_2O, Warm → Phenol + N_2 + HCl

4. From Cumene

Cumene → O_2 → Cumene hydroperoxide → H^+, H_2O → Phenol + CH_3COCH_3

Ethers

1. By dehydration of alcohols

$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$

2. Williamson synthesis

$RX + R'ONa \longrightarrow R\text{–O–}R' + NaX$

Phenol + NaOH → Sodium phenoxide → R-X → Ether

Commercially important alcohols

Ethers

(i)Physical :
- C–O bonds are polar.
- Boiling points comparable to those of alkanes.
- Solubility in water as alcohols.

(ii)Chemical : $R\text{–O–}R + HX \longrightarrow RX + R\text{–}OH$

Anisole → Br_2 in Ethanoic acid → 4-Bromoanisole + 2-Bromoanisole

Anisole → H_2SO_4, HNO_3 → 4-Nitroanisole + 2-Nitroanisole

Friedel-Crafts reaction :

Anisole + CH_3Cl, Anhyd.$AlCl_3$, CS_2 → 4-Methylanisole + 2-Methylanisole

Anisole + CH_3COCl, Anhyd.$AlCl_3$ → 4-Methoxyacetophenone + 2-Methoxyacetophenone

- **Methanol (Wood spirit) :** Used as solvent in paint, varnishes and making formaldehyde.
- **Ethanol :** Used as solvent in paint industry and preparation of a number of carbon compounds.

Trace the Mind Map

First Level · Second Level · Third Level

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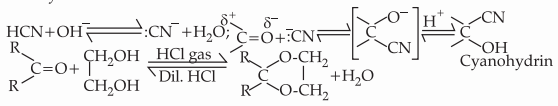
ALDEHYDES AND KETONES:

(i) Physical:

Boiling points are higher than hydrocarbons and ethers of comparable molecular masses and lower than alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

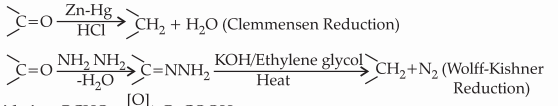
(ii)Chemical :Nucleophilic addition reactions :

Aldehydes are more reactive than ketones due to steric and electronic reasons.



Reduction : (a) To alcohols – aldehydes and ketones reduce to primary and secondary alcohols respectively by $NaBH_4$ or $LiAlH_4$.

(b) To hydrocarbons –



Oxidation: $RCHO \xrightarrow{[O]} R\text{–}COOH$ Silver mirror

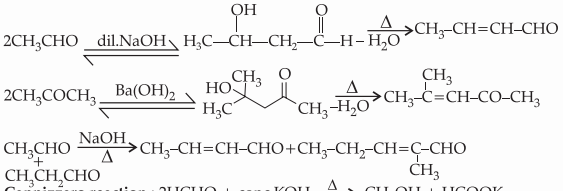
Tollen's test : $RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag\downarrow + 2H_2O + 4NH_3$

Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O\downarrow + 3H_2O$ Red brown ppt

Haloform reaction:

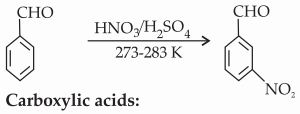
$R\text{–}\overset{O}{\overset{\|}{C}}\text{–}CH_3 \xrightarrow{NaOX} R\text{–}\overset{O}{\overset{\|}{C}}\text{–}ONa + CHX_3$ (X = Cl, Br, I)

Reactions due to α - hydrogen:



Cannizzaro reaction : $2HCHO + \text{conc } KOH \xrightarrow{\Delta} CH_3OH + HCOOK$

Electrophilic substitution reaction:



Carboxylic acids:

(i) Physical: Higher boiling points than aldehydes, ketones or alcohols. Solubility decreases with increasing number of C atoms.

(ii)Chemical : $2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$

Forms corresponding anhydride on heating with mineral acids

$RCOOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^-\ {}^+NH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$

$RCOOH \xrightarrow[H_3O^+]{B_2H_6} RCH_2OH$

$RCOONa \xrightarrow[NaOH \& CaO]{Heat} R\text{–}H + Na_2CO_3$

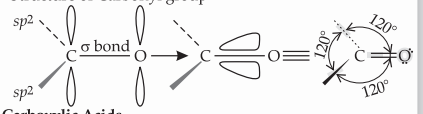
$RCH_2COOH \xrightarrow[H_2O]{X_2/Red\ P} R\text{–}\underset{X}{CH}\text{–}COOH$ (HVZ reaction) (X=Cl, Br)

1. **Aldehydes and Ketones**

Common names :

- Replace corresponding carboxylic acids with aldehyde.
- Alkyl phenyl ketones by adding acyl group as prefix to phenone.
- IUPAC names :
- Replacing –e with –al and –one as required.

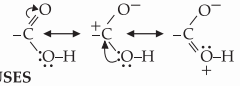
Structure of Carbonyl group



2. **Carboxylic Acids**

Common names : end with –ic

- IUPAC names : replace –e in the corresponding alkane with –oic acid.
- Structure of Carboxyl Group



3. **USES**

(a) Carboxylic acids

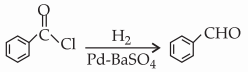
- Methanoic acid in rubber, textile, dyeing, leather industries.
- Ethanoic acid as solvent.
- Higher fatty acids in manufacture of soaps and detergents.

(b) Aldehydes of ketones

- As solvents.
- Starting materials and reagents for synthesis of products.

ALDEHYDES:

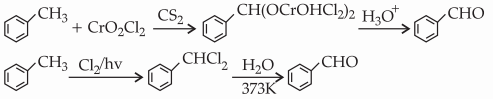
1. From acyl chloride



2. From nitriles and esters : Stephen reaction

$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} R\ CHO$

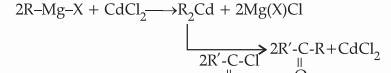
3. From hydrocarbons : Etard reaction



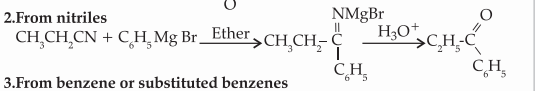
Gattermann – Koch reaction 

KETONES:

1.From acyl chloride



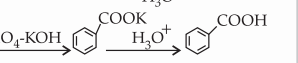
2.From nitriles



3.From benzene or substituted benzenes

Carboxylic Acids:

1.From primary alcohols and aldehydes $RCH_2OH \xrightarrow[H_3O^+]{alk.\ KMnO_4} RCOOH$

2.From alkylbenzenes 

3.From nitriles and amides $R\text{–}CN \xrightarrow[H_2O]{H^+ or\ OH^-} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[\Delta]{H^+ or\ OH^-} RCOOH$

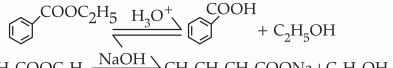
4.From Grignard reagents $R\text{–}Mg\text{–}X + CO_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^-MgX^+ \xrightarrow{H_3O^+} RCOOH$

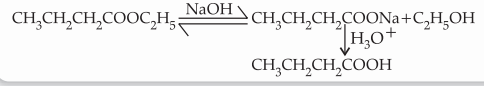
5.From acyl halides and anhydrides

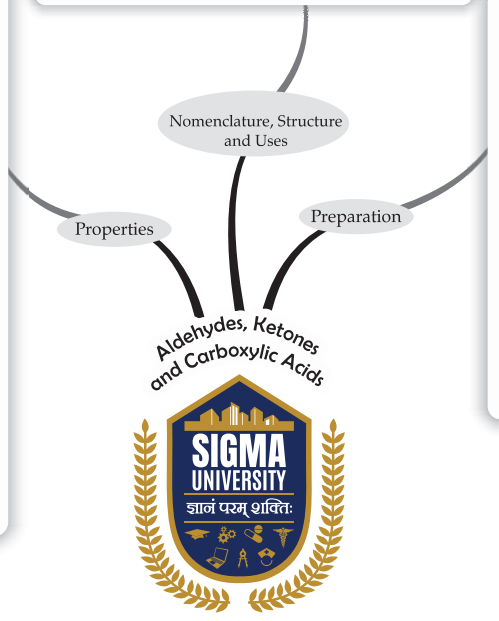
$RCOCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

6.From esters







Trace the Mind Map

First Level · Second Level · Third Level

Amines

Chemical reactions

(i) Basic character of amines

- React with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- React with base to regenerate parent amines
  $RN^+H_3X^- + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : $1^\circ > 2^\circ > 3^\circ$

(ii) $C_2H_5-NH+CH_3-\underset{\underset{O}{\|}}{C}-Cl \xrightarrow[\text{Base}]{} C_2H_5-N(C_2H_5)-\underset{\underset{O}{\|}}{C}-CH_3 + HCl$

(iii) Carbylamine reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

(v) $C_6H_5-\underset{\underset{O}{\|}}{S}-Cl + H_2N-C_2H_5 \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{S}-H-C_2H_5 + HCl$

(vi) Electrophilic substitution

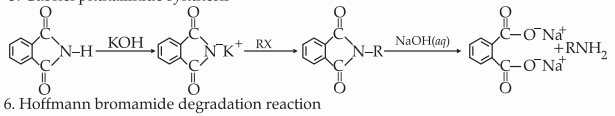
$C_6H_5NH_2 + 3Br_2 \xrightarrow{Br_2/H_2O} 2,4,6\text{-}Tribromoaniline + 3HBr$

$C_6H_5NH_2 \xrightarrow[288K]{HNO_3,H_2SO_4}$ *p*-nitroaniline (51%) + *m*-nitroaniline (47%) + *o*-nitroaniline (2%)

$C_6H_5NH_2 \xrightarrow[453\text{-}473K]{H_2SO_4} C_6H_5N^+H_3HSO_4^- \rightleftharpoons$ sulphanilic acid (SO_3H, NH_2) $\rightleftharpoons$ $C_6H_5N^+H_3SO_3^-$

Preparation

1. Reduction of nitro compounds: $C_6H_5NO_2 \xrightarrow[\text{Ethanol}]{H_2/Pd} C_6H_5NH_2$; $C_6H_5NO_2 \xrightarrow[\text{or Fe+HCl}]{Sn+HCl} C_6H_5NH_2$
2. Ammonolysis of alkyl halides: $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\,\bar{X}$
3. Reduction of nitriles: $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2NH_2$
4. Reduction of amides: $R-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$
5. Gabriel phthalimide synthesis



6. Hoffmann bromamide degradation reaction

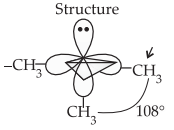
$R-\underset{\underset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Physical properties

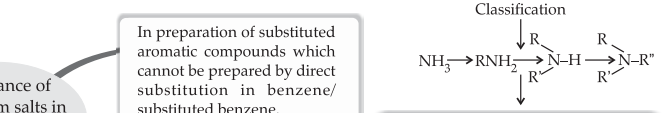
- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association.
- Boiling point : primary > secondary > tertiary

Derivatives of ammonia, obtained by replacement of one, two or all the three H-atoms by alkyl and/or aryl groups

Structure



Classification



Nomenclature

Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group.

IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Importance of diazonium salts in synthesis of aromatic compounds

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Diazonium Salts (RN_2X)

Preparation :

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction: $ArN_2^+X^- \xrightarrow[Cu_2Br_2/HBr]{Cu_2Cl_2/HCl} ArCl + N_2$; $\xrightarrow{} ArBr + N_2$; $\xrightarrow[CuCN/KCN]{} ArCN + N_2$

Gattermann reaction :

$ArN_2^+X^- \xrightarrow[Cu/HBr]{Cu/HCl} ArCl + N_2 + CuX$; $\xrightarrow{} ArBr + N_2 + CuX$

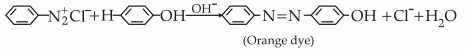
(ii) $ArN_2^+Cl^- + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2^+Cl^- + HBF_4 \longrightarrow ArN_2^+BF_4^- \xrightarrow{\Delta} ArF + BF_3 + N_2$

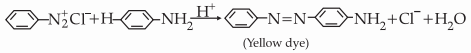
(iv) $ArN_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2^+Cl^- + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) **Coupling reaction :**



(Orange dye)



(Yellow dye)

Trace the Mind Map
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Biomolecules

Proteins

-(Polymers of amino acids)
-Amino acids contain $-NH_2$ and –COOH group.

Classification :

- **On the basis of relative number of $-NH_2$ and –COOH group:**
  - (i) Neutral : Equal number of $-NH_2$ and –COOH group.
  - (ii) Basic : More number of $-NH_2$ than –COOH group.
  - (iii) Acidic : More number of –COOH than $-NH_2$ group.
- **On the basis of place of synthesis :**
  - (i) Essential – cannot be synthesized in the body.
  - (ii) Non-essential – synthesized in the body.
- **On the basis of shape :**
  - (I) Fibrous : Fibre-like structure
  - (ii) Globular : Spherical

Structure : $H_2N-CH_2-\boxed{CO-NH}-CH(CH_3)-COOH$ (Peptide linkage)

Denaturation of protein :
When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity.

Carbohydrates

Optically active polyhydroxy aldehydes or ketones or compounds which produce units with specific functional groups on hydrolysis.

- **Classification :**

(I) **Monosaccharides :** (Aldehyde group – aldose, keto group –ketose)
Glucose : Preparation :

(a) **From sucrose :** $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$ (Sucrose)

(b) **From starch :** $(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

- **Structure :** CHO–(CHOH)$_4$–CH$_2$OH

HI, Δ → $CH_3CH_2CH_2CH_2CH_2CH_3$

NH_2OH → CH=N–OH, (CHOH)$_4$, CH$_2$OH

HCN → CH(CN)–OH, (CHOH)$_4$, CH$_2$OH

Br_2 Water → COOH, (CHOH)$_4$, CH$_2$OH

Acetic anhydride → CHO, (CH–O–C(=O)–CH_3)$_4$, CH_2–O–C(=O)–CH_3

Oxidation → COOH, (CHOH)$_4$, COOH

Cyclic Structures

Pyran

α–D–(+)–Glucopyranose

β–D–(+)–Glucopyranose

Structure of Fructose

Furan

α–D–(–)–fructofuranose

β–D–(–)–fructofuranose

(II) **Disaccharides :** (Sucrose, maltose) Linkage between 2 monosaccharides– Glycosidic linkage
(III) **Polysaccharides :** Large number of monosaccharides units joined by glycosidic linkages. e.g.,
(a) Starch : Polymer of α–glucose with two components amylose and amylopectin
(b) Cellulose
(c) Glycogen

Importance :
- Form a major portion of food.
- As storage molecules.
- Cellulose forms cell wall of bacteria and plants.
- Raw materials for industries like textiles, paper, lacquers and breweries.

Vitamin

Organic compounds required in diet in small amounts to perform specific biological functions for maintenance and growth.

Classification :

(i) **Fat soluble :** Soluble in fats and oils but insoluble in water. (Vitamins A,D,E and K)
(ii) **Water soluble :** B group and vitamin C are soluble in water.

Nucleic Acids

Chromosomes : Particles in nucleus responsible for heredity. Chromosomes are made up of proteins and nucleic acid.
Two types : Deoxyribonucleic acid (DNA), ribonucleic acid (RNA)
Composition : In DNA, sugar is β–D–2–deoxyribose whereas in RNA is β–D–ribose. DNA contains A,G,C,T whereas RNA has A,G,C,U.
Structure :
Nucleoside : Formed by attachment of a base to 1′ of sugar
Nucleotide : Formed by link to phosphoric acid at 5′ of sugar.

Base–Sugar–Phosphate–[Base–Sugar–Phosphate]–Base–Sugar–

Types of RNA : m–RNA, r–RNA, t–RNA

Biological Functions :
- Chemical basis of heredity.
- Responsible for identity of different species of organisms.
- Nucleic acids are responsible for protein synthesis in cell.

DNA Fingerprinting : Unique sequence of bases on DNA

A sequence of bases on DNA is unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment. DNA fingerprinting is now used
(i) in forensic laboratories for identification of criminals.
(ii) to determine paternity of an individual.
(iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children.
(iv) to identify racial groups to rewrite biological evolution.

Enzymes

Globular proteins specific for particular reaction and for particular substrate. Mechanism : Reduces the magnitude of activation energy

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