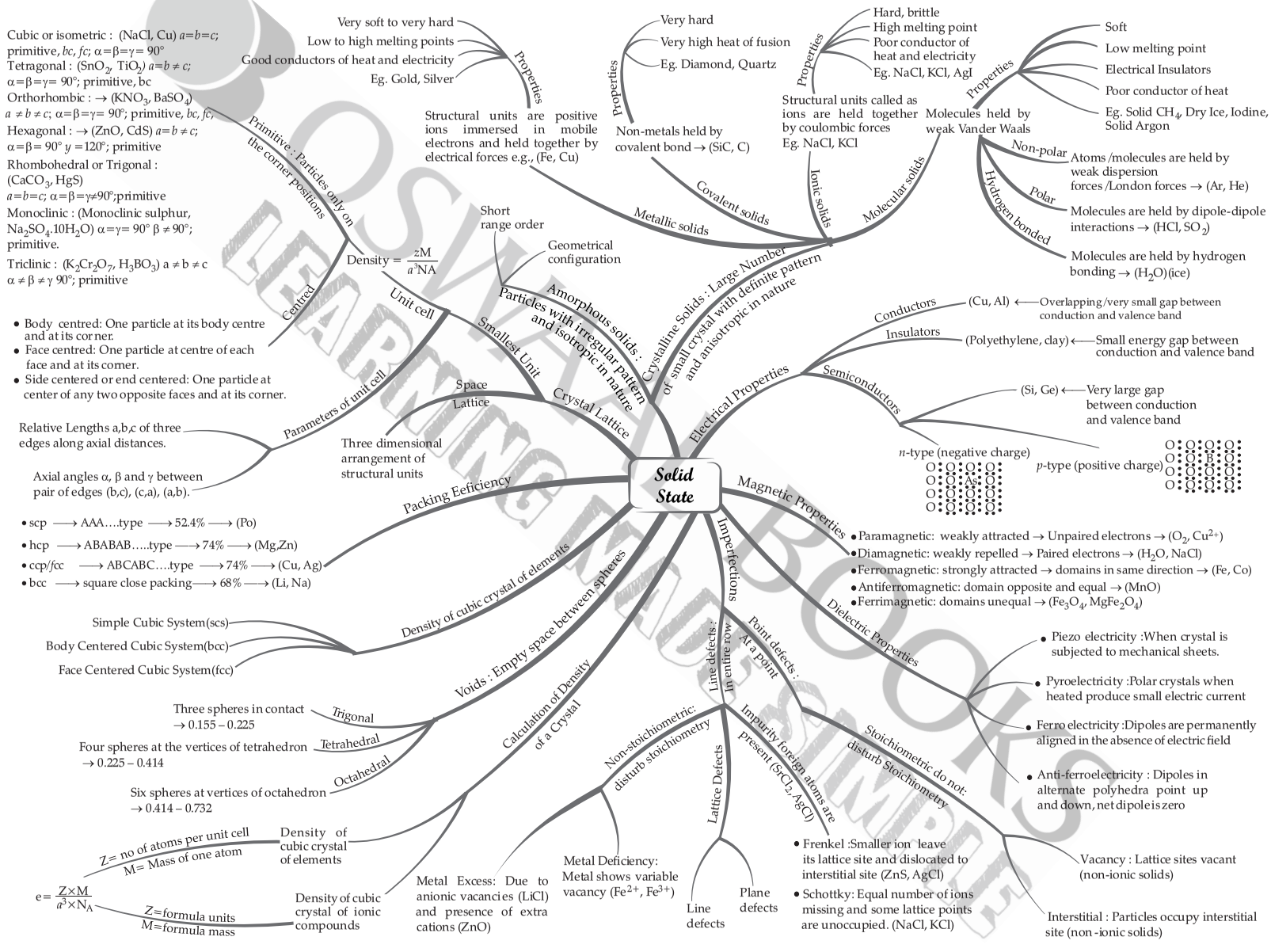
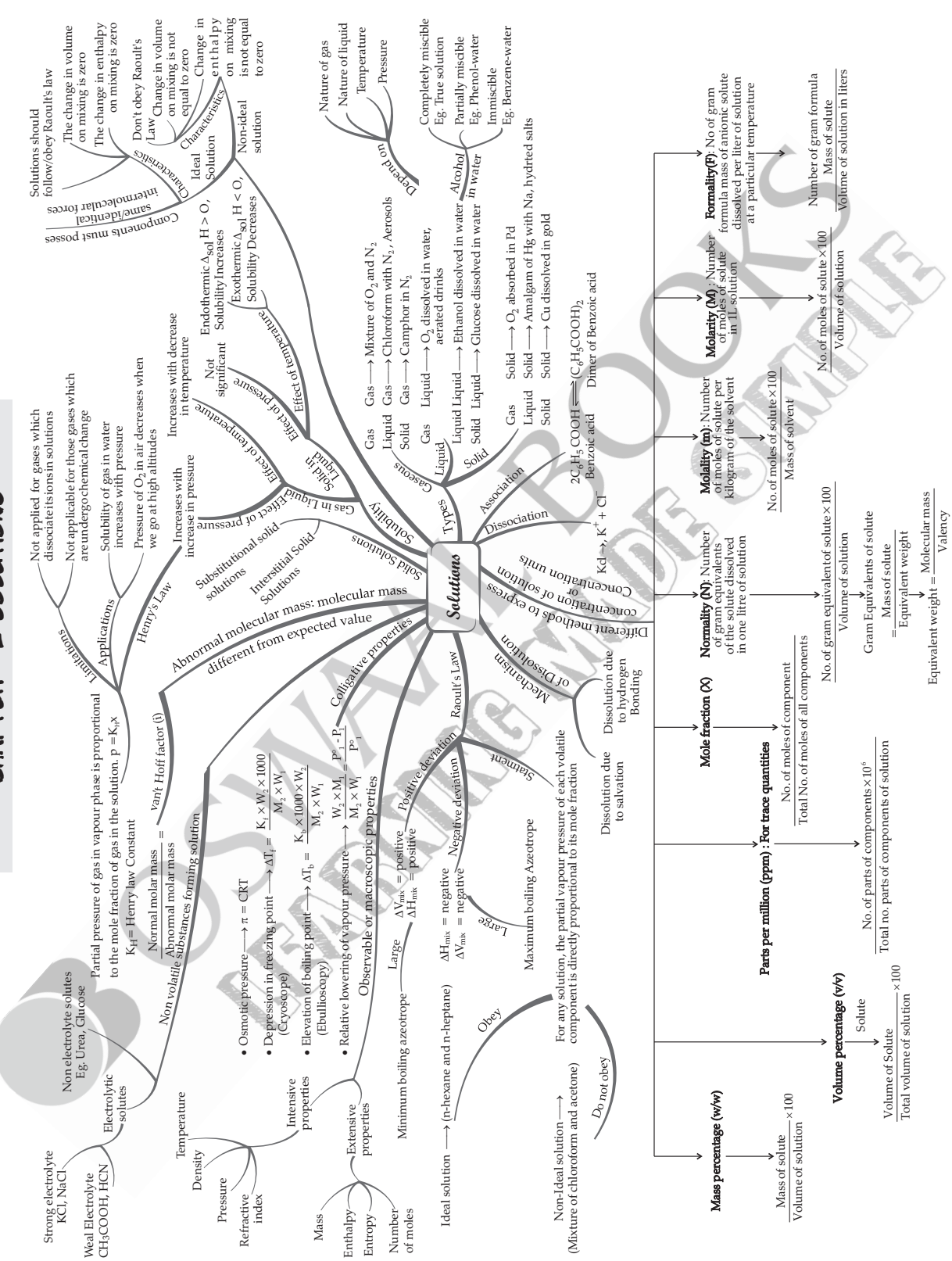
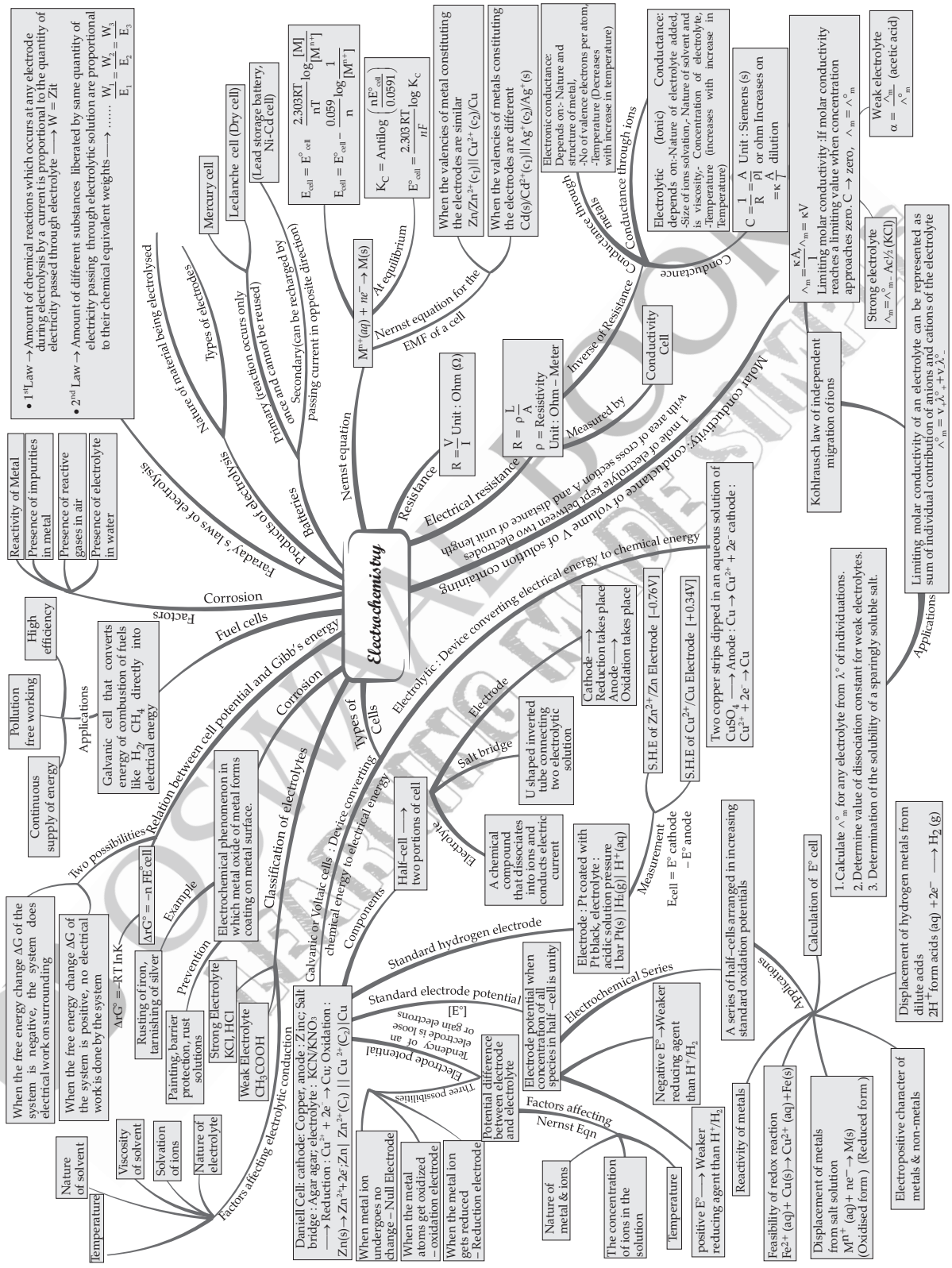
CHAPTER - 1 SOLID STATE







CHAPTER - 4 CHEMICAL KINETICS

Chemical Kinetics

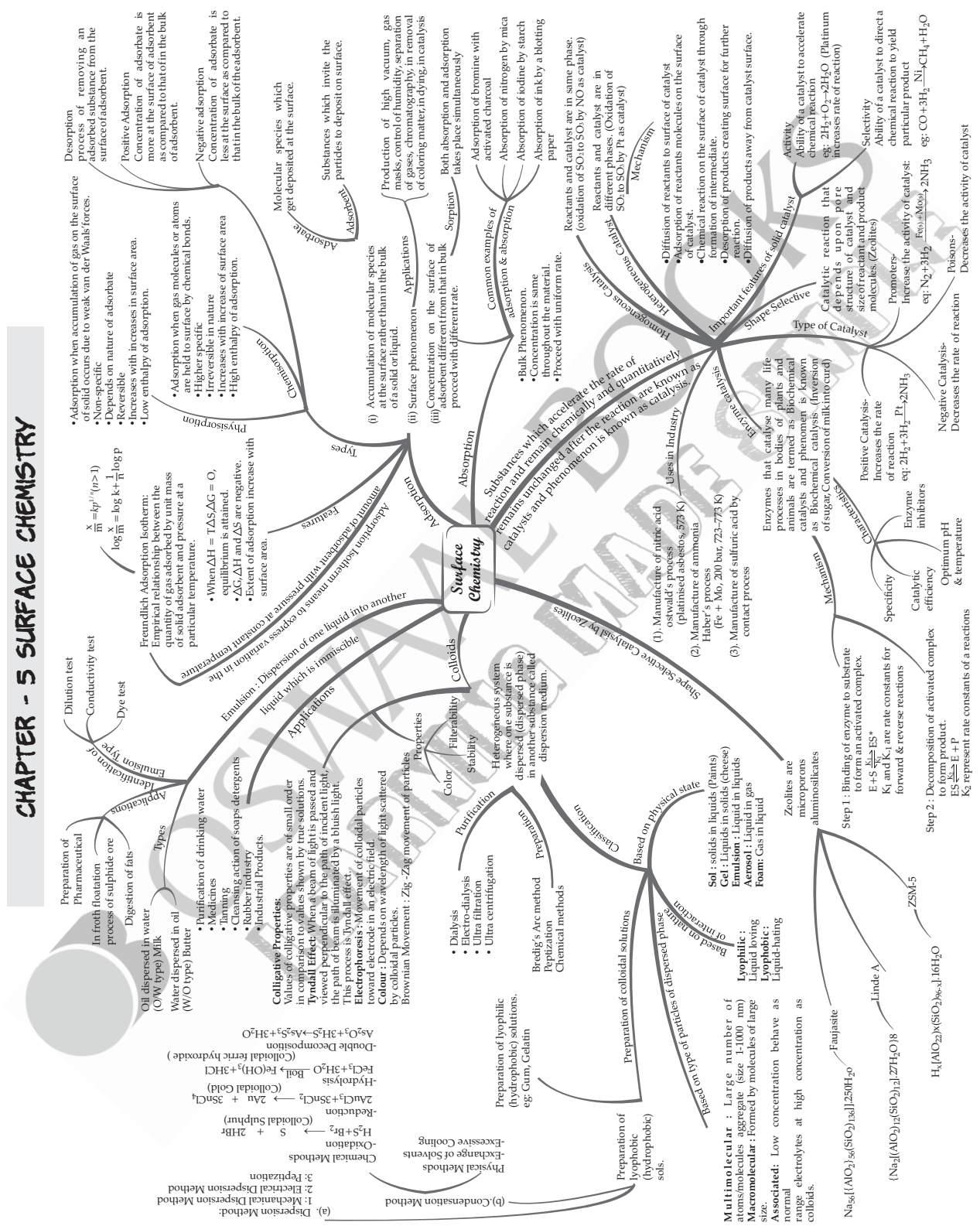
- Collision Theory: Rate of reaction depends on the collision frequency and effective collisions.
  - Collision Frequency
    - Number of collisions per unit volume of reaction mixture
      $Rate = Z_{AB}e^{-Ea/RT}$
    - Activation energy
      - E_a and proper orientation of the molecules determine the criteria for an effective collision.
      - Activation Energy = Threshold energy - Average energy possessed by reactant molecule
        $Ea = E_{threshold} - E_{reactants}$
      - $Rate = PZ_{AB}e^{-Ea/RT}$
        P is Steric or Probability factor
    - Effective Collision
      - Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.
      - They over come → • Energy barrier
        → • Orientation barrier
- Molecularity of a Reaction
  - Molecularity of Elementary Reaction
    $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$
    molecularity = 1, unimolecular reaction]
  - Molecularity of Complex reaction
    $2FeCl_3 + 6KI \rightarrow 2FeI_2 + 6KCl + I_2$
  - Pseudo Unimolecular Reactions
    $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
    (Ethyl acetate) (In excess)
    $Rate = K[CH_3COOC_2H_5]$
- Order of a Reaction
  - Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.
  - Sum of powers of concentration of the reactants in the rate law.
- Rate of Chemical Reaction
  - Change in concentration of reactants or products in unit time; Unit : mol $L^{-1}s^{-1}$ or atm s^{-1}
    - Average Rate of reactions $A \rightarrow B$
      - In terms of decrease of [A] Concentration
      - In terms of increase in the concentration of B
      - Reactions involving the same stoichiometric coefficients of reactants and products
      - Reactions involving different stoichiometric coefficients of reactants and products
      - $K[CH_3COOC_2H_5]$
      - Formation of Ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
      - Decomposition of N_2O_5 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2$
      - Appearance of products or disappearance of reactants over a long time interval.
        $r_{av} = \frac{d[P]}{dt} = slope$
        $r_{av} = \frac{-d[R]}{dt} = -slope$
    - Instantaneous Rate
      - Rate of change in concentration of reactant/product at a particular time
        $r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$
    - $R \rightarrow P$
      - Rate of disappearance of R
        $= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = \frac{-\triangle[R]}{\triangle t}$
      - Rate of appearance of P
        $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\triangle[P]}{\triangle t}$
    - Factors Influencing
      - **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.
      - **Presence of Catalyst :** Increases with a catalyst.
      - **Surface Area :** Greater is the surface area, faster is the rate of reaction.
      - Activation Energy : Lower the activation energy,
    - 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.
        $aA + bB \rightarrow cC + dD$
        $Rate = K[A]^x[B]^y = \frac{d[R]}{dt}$
    - Rate Constant: Rate of reaction when concentration of each of the reactant in unity.

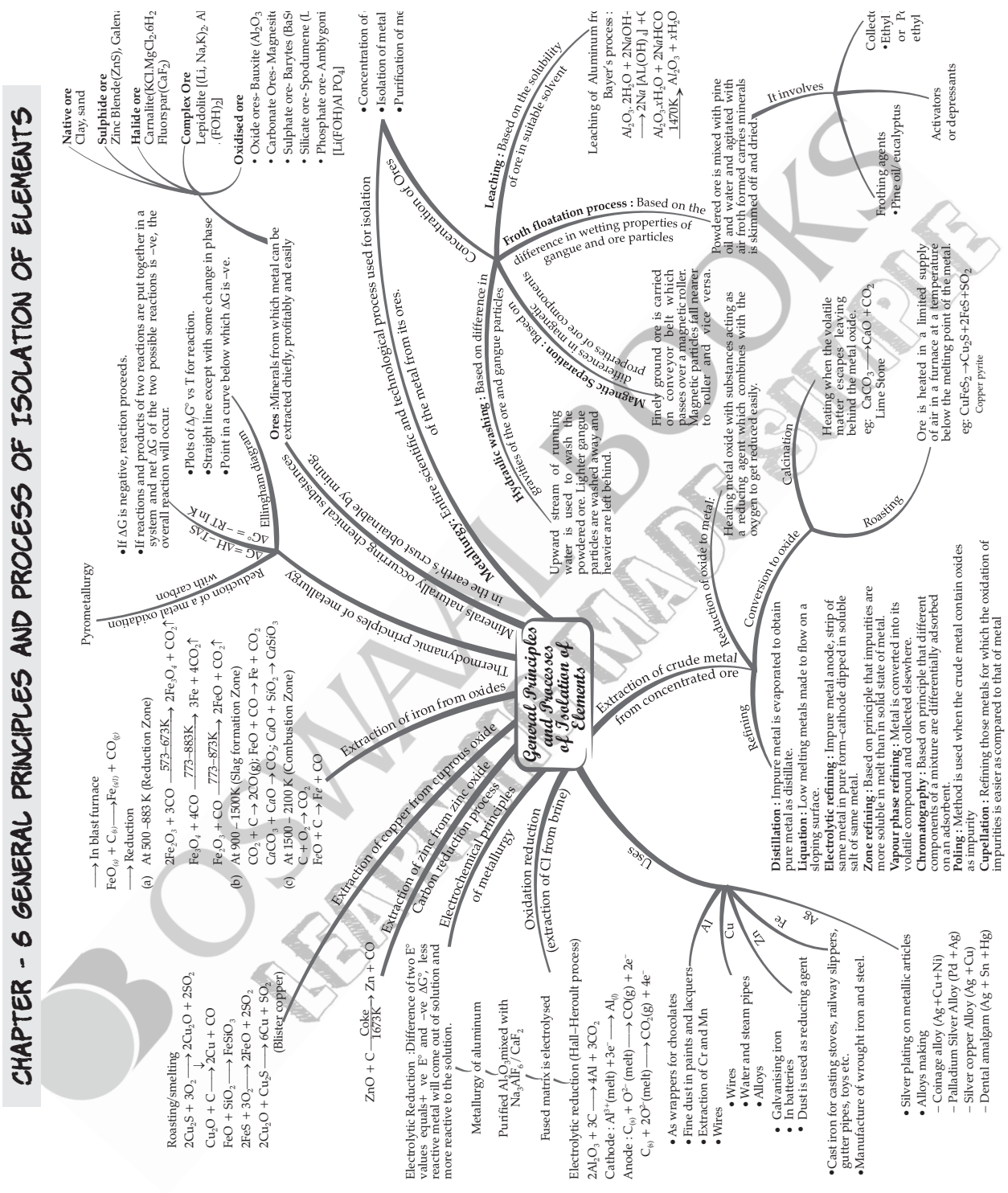
Order	Unit
0	$mol L^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}Ls^{-1}$
3	$mol^{-2}L^2s^{-1}$

- Arrhenius Equation
  - $K = Ae^{-Ea/RT}$
  - $\log k = \log A - \frac{E_a}{2.303RT}$
  - $\log = \frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1T_2}\right]$
- Methods to determine the concentration
  - Graphical Method
    $Rate \propto (A)^n$
    $Rate = K(a)^n$
  - Initial Rate Method
  - Integrated Rate Law Method
- Integrated Rate Equation
  - Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

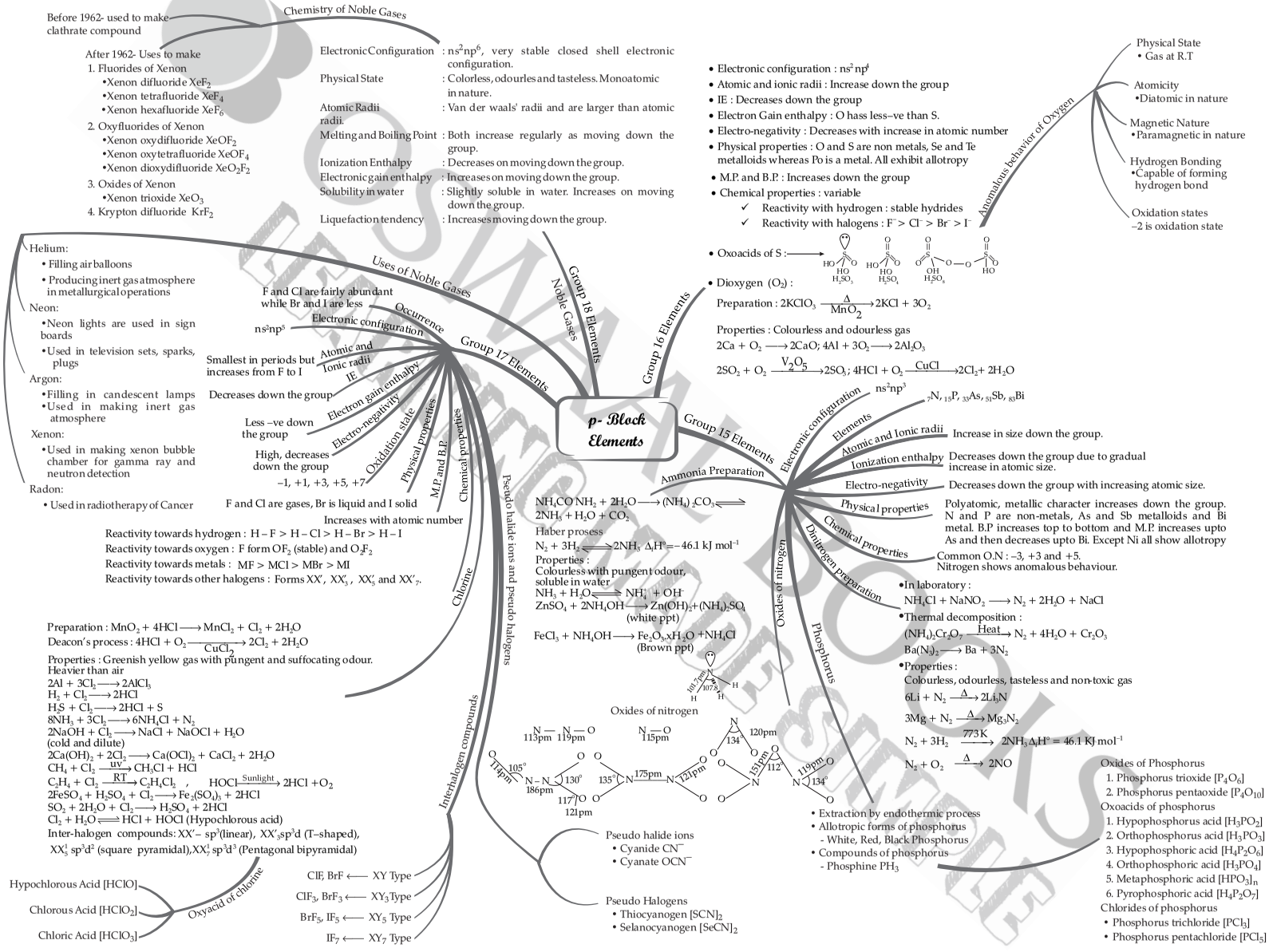
Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	$mol\ L^{-1}s^{-1}$
1	$kt = \ln\{[R]_0/[R]\}$	In[R] vs t	s^{-1}

- Pseudo First Order Reaction
  - Are not truly of first order but under certain conditions behave as first order reaction
  - Acid hydrolysis of ethyl acetate
  - Inversion of sugar
- First Order Reaction
  - Decomposition of Ethyl alcohol
    $C_2H_5Cl \rightarrow C_2H_4 + HCl$
    $Rate = K[C_2H_5Cl]$
    Order of reaction=1
  - Decomposition of nitrogen pentoxide
    $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$
    $Rate = K(N_2O_5)$
    Order of reaction=1
- Second Order Reaction
  - Decomposition of Nitrogen dioxide NO_2
    $2NO_2 \rightarrow 2NO + O_2$
    $Rate = K[NO_2]$,
    Order of reaction=2
- Third Order Reaction
  - Reaction between NO and Cl_2
    $2NO + Cl_2 \rightarrow 2NOCl_2$
    $Rate = K[NO][Cl]$
    Order of reaction=2+1=3
- Half-life of a Reaction
  - Time in which the concentration of a reactant is reduced to one half of its initial concentration
    - 1st Order
      $t_{1/2} = \frac{0.693}{K}$
    - 0 Order
      $t_{1/2} = \frac{[R]^0}{2K}$
- Reactions of fractional order
  - Decomposition of Acetaldehyde
    $CH_3CHO \rightarrow CH_4 + CO$
    $Rate = K[CH_3CHO]^{3/2}$
    $Order = 3/2 = 1.5$
- Zero order reaction
  - Photochemical combination of H_2 and Cl_2 over the surface of water
    $H_2 + Cl_2 \rightarrow 2HCl$
    $Rate = K[H_2]^0[Cl_2]^0$
    $Order = 0$





CHAPTER - 7 p-BLOCK ELEMENTS



CHAPTER - 8 d-AND f-BLOCK ELEMENTS

d– and f– Block Elements

d– Block transition elements groups 3–12

- Position : Between s–and p–blocks
- Classification off transition elements
  - (i) First transition Series or 3d series -from Sc to Zn
  - (ii) Second transition series or 4d series -from Y to cd
  - (iii)Third transition series or 5d series -from Lu, Hg to Hf
  - (iv) Fourth transition series or 6d series -from Ac to those having atomic number 104 above
- 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 imperfect shielding of one e^- by another in same set of orbitals.
- Ionisation enthalpies : Increases from left to right
- Oxidation states : Variable ;higher ON 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.
- Alloy formation : Due to similar atomic sizes.

Oxides and oxoanions of metals

- Potassium dichromate $K_2Cr_2O_7$

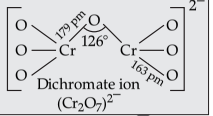
  Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

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

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

  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^-



Dichromate ion $(Cr_2O_7)^{2-}$

- Potassium permanganate $KMnO_4$

  Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2KMnO_4 + 2H_2O$

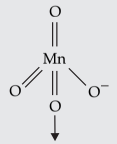
  $3\,MnO_4^{2-} + 4H^+ \rightarrow 2\,MnO_4^- + MnO_2 + 2H_2O$

  $2Mn^{2+} + 5S_2O_3 + 8H_2O \rightarrow 2\,MnO_4^- + 10\,SO_4^{2-} + 16H^+$

  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^-



Tetrahedral MnO_4^- (purple ion)

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.

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

Actinoids

- Electronic : configuration $[Rn]5f^{1-14}\ 6d^{0-2}7s^2$
- Ionic sizes : Gradual decrease along the series
- Oxidation states : Most common is +3. They show ON 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.

Uses of Actinoids

- Thorium and its compound are used in nuclear chemistry.
- Uranium and plutonium are use as fuels in nuclear reactors.
- Thorium salt are used in the treatment of cancer.

f– Block Transition Elements

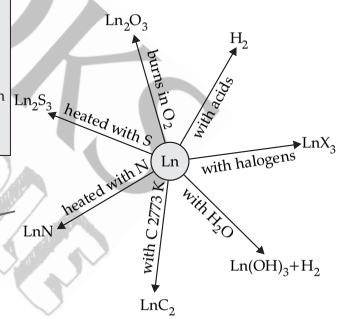
Lanthanoids

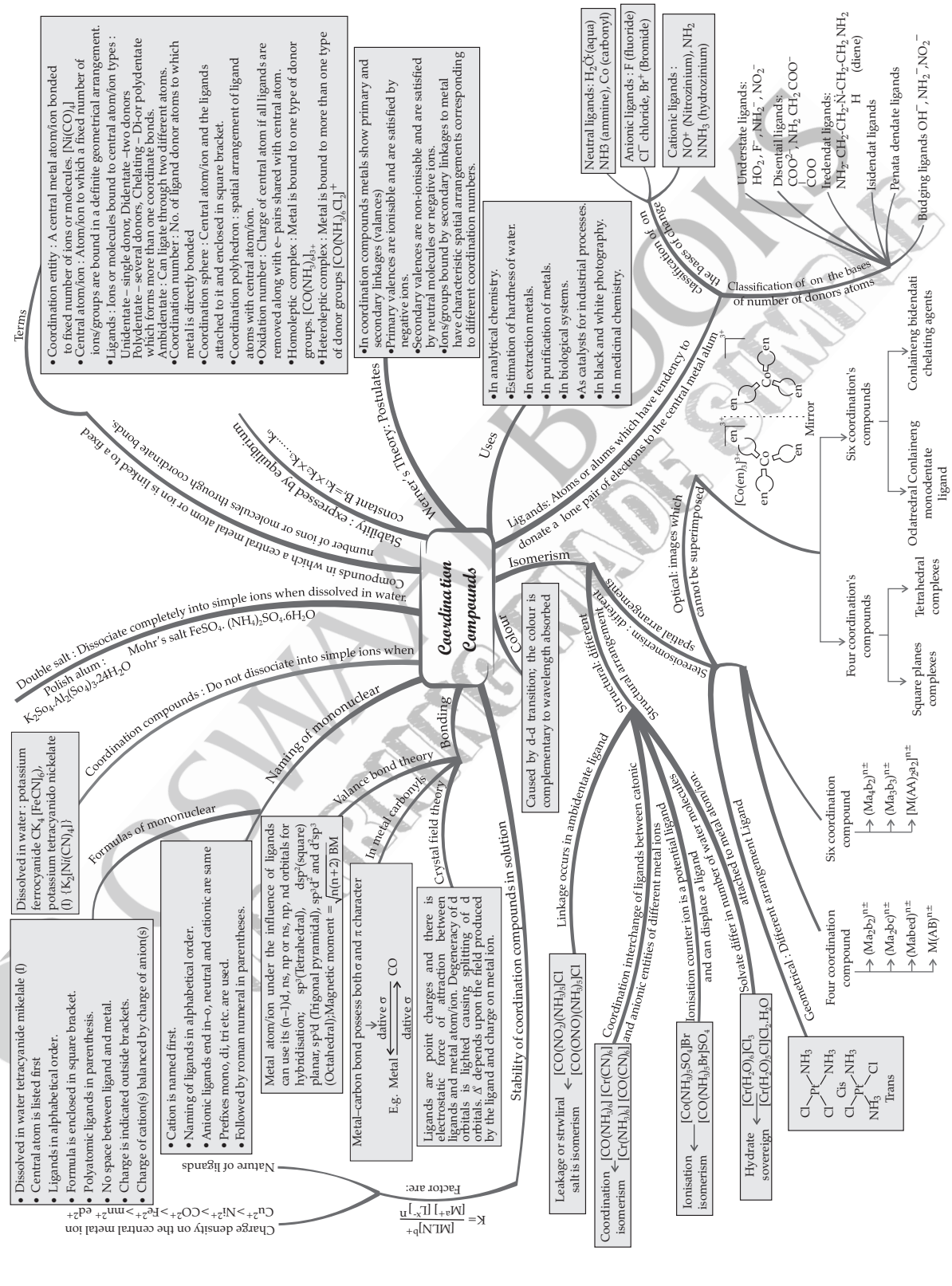
- Electronic configuration $4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Atomic and ionic sizes
  Decreases from La to Lu
- Oxidation states
  Most common is +3. Some elements exhibit +2 and +4.
- General characteristics
  - •Silvery while soft metals and tarnish rapidly in air.
  - •Hardness increases with increasing 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

Uses of Lanthanoids

- Misch metals containing 30-35% of Ce are used as reducing agents.
- Mg- alloys are with 30% of misch metal and 1% zinc for making jet planes.
- Cerium phosphate used as catalysts in petroleum industry.
- Nd_2O_4 and Pr_2O_3 are used for coloring glass

Chemical Properties





CHAPTER - 10 HALOALKANES AND HALOARENES

Haloalkanes and Haloarenes

Introduction

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

- (a) Dextro (+/d)
- (b) laevo (–/l)

Haloalkanes

Classification

- Aliphatic Halogen Compounds
  - Haloalkanes: $H-\underset{H}{\overset{H}{C}}-Cl$ (Cloro methane)
  - Alkyl halides
    - (i) 1° Alkylhalide eq. CH_3-Cl
    - (ii) 2° Alkyl halide eq. $CH_3-\underset{CH_3}{\overset{H}{C}}-Br$
    - (iii) 3° Alkyl halide eq. $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$
  - Haloalkenes: $CH_2=CH-Cl$
  - Haloalkenes: $H-C\equiv C-Br$
- Aromatic Halogen Compounds
  - Nuclear halogen derivative: Chloro Benzene, Bromo Benzene
  - Sidechain halogen derivative: Benzyl Chloride (CH_2Cl), Benzal Chloride ($CHCl_2$)

Properties

- No. of halogen atoms
  - C_2H_5X — Monohaloalkane
  - CH_2X, CH_2X — Dihaloalkane
  - Monohaloarene, Dihaloarene, Trihaloarene
- 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 polarized
- Compounds containing sp C–X bond
  - H—C≡ C–Cl Cloroethyne

Preparation

- From alcohol :
  - $R-OH + HCl \xrightarrow{ZnCl_2} R-Cl + H_2O$
  - $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$
  - $ROH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$
- From hydrocarbons :
  - (a) By free radical halogenations
    - $CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
  - (b) By electrophilic substitution
    - $C_6H_5CH_3 + X_2 \xrightarrow[Dark]{Fe} o\text{-}XC_6H_4CH_3 + p\text{-}XC_6H_4CH_3$
  - (c) Sand meyer's reaction
    - $C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HX} C_6H_5N_2X \xrightarrow{Cu_2X_2} C_6H_5X + N_2$
  - (d) From alkenes
    - $>C=C< + HX \rightarrow >\underset{X}{C}-\underset{H}{C}<$
    - $H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2-CH_2Br$
- Halogen exchange :
  - $R-X + NaI \rightarrow R-I + NaX$

Properties

- Physical : Colourless, volatile, sweet smell.
  - Lower members are gases at room temperature while higher are solids. B.P : RI >R Br > 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
    - $Nu^- + >\overset{\delta+}{C}-\overset{\delta-}{X} \longrightarrow >C- Nu + X^-$
    - For S_N2 reaction: Tertiary, Secondary, Primary
    - For S_N1 reaction
  - (b) Elimination reaction
    - $>C-\underset{H}{C}-\xrightarrow{B:} >C=C< + B-H + X^-$
    - B = Base; X = Leaving group
  - (c) Reaction with metals
    - $CH_3CH_2Br + Mg \longrightarrow CH_3CH_2MgBr$
    - Wurtz reaction : $2RX + 2Na \xrightarrow{\text{Dry ether}} R-R + 2NaX$

Isomerism :

- (1) Chain isomerism (C_4H_9Cl) :
  - $CH_3-CH_2-CH_2-CH_2-Cl$ (1-Chlorobutane)
  - $CH_3-\underset{CH_3}{CH}-CH_2-Cl$ (1-Chloro 2-methylpropane)
  - $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$ (2-Chloro 2-methylpropane)
- (2) Position isomerism : (C_3H_7Cl) :
  - $CH_3-CH_2-CH_2Cl$ (1-Chloro propane)
  - $CH_3-\underset{Cl}{CH}-CH_3$ (2-Chore propane)

Polyhalogen compounds

- Ethyl Bromide (C_2H_5Br)
  - Preparation: $C_2H_5OH + KBr + H_2SO_4 \xrightarrow{Heat} C_2H_5Br + KHSO_4 + H_2O$
  - Physical properties: colorless liquid boils at 312.3 K.
  - Chemical properties:
    - $CH_3CH_2Br \xrightarrow[Ether]{Mg} CH_3-CH_2-Mg-Br$ Grignard reagent
    - $CH_3CH_2Br \xrightarrow{KOH} CH_3CH_2OH$ Ethyl alcohol
    - $CH_3CH_2Br \xrightarrow[Ether]{Li} CH_3CH_2Li$ Ethyl lithium
- Polyhalogen compounds
  - Chloroform or $CHCl_3$
  - Preparation: $CH_4 \xrightarrow[H_2]{Cl_2} CH_2Cl_2 + CH_3Cl + CHCl_3 + CCl_4$
  - Physical Preparation: Colorless heavy liquid.
  - Chemical properties:
    - $CH_3CH_2Br \xrightarrow[\text{Sun light}]{O_2} COCl_2 + HCl$ Phosgene
    - $CH_3CH_2Br \xrightarrow[Zn+HCl]{H_2} CH_2Cl_2 + HCl$ Methylene chloride
- Iodoform or Triiodomethane CHI_3
  - Some reactions
    - $CHI_3 \xrightarrow[HI+P_4]{2H} CH_2I_2 + HI$ Methylene Iodide
    - $CHI_3 \xrightarrow[Heat]{6Ag} H-C\equiv C-H + 6AgI$ Ethyne
- Carbon Tetrachloride CCl_4
  - Some reactions
    - $CCl_4 \xrightarrow[SbCl_5]{2HF} CCl_2F_2 + 2HCl$ Dichlorodifloromethane (Freon)
    - $CCl_4 \xrightarrow{H_2O} COCl_2 + 2HCl$ Phosgene

Haloarenes

- Reactions :
  - (a) Nucleophilic substitution
    - (i) Resonance effect
    - (ii) Hybridization of C – X bond in : Haloalkane –sp^3; Haloarence –sp^3
    - (iii) Phenyl cation unstabilised by resonance
  - (b) Electrophilic substitution
    - Chlorobenzene $\xrightarrow{Anhyd.FeCl_3, +Cl_2}$ o- and p-dichlorobenzene
    - Chlorobenzene $\xrightarrow[conc.\ H_2SO_4]{HNO_3}$ o- and p-nitrochlorobenzene
    - Chlorobenzene $\xrightarrow[\Delta]{conc.\ H_2SO_4}$ o- and p-chlorobenzenesulphonic acid
    - Friedel – Crafts reaction
      - Chlorobenzene $\xrightarrow[Anhyd.\ AlCl_3]{+CH_3Cl}$ o- and p-chlorotoluene
      - Chlorobenzene $\xrightarrow[Anhyd.\ AlCl_3]{+H_3C-\overset{O}{\overset{\|}{C}}-Cl}$ o- and p-chloroacetophenone
  - (c) Reaction with metals
    - Wurtz – Fittig reaction: $C_6H_5X + 2Na + RX \xrightarrow{Ether} C_6H_5R + NaX$
    - Fittig reaction: $2C_6H_5X + 2Na \xrightarrow{Ether} C_6H_5-C_6H_5 + 2NaX$

Uses

- Manufacture of refrigerants and propellants.
- Cleaning fluid
- Solvent for fats, alkaloids, I etc.
- Production of Freon
- For aerosol propellants, refrigeration and air conditioning purposes
- Paint remover
- Propellant in aerosols
- Metal cleaning and finishing solvent.

Benzene Hexachloride (BHC) or ($C_6H_6Cl_6$)

- Benzene $\xrightarrow[Light]{UV, +3Cl_2}$ Benzene Hexachloride

Chloroform

- Chloral $\xrightarrow{conc.\ H_2SO_4, -H_2O}$ Chlorobenzene

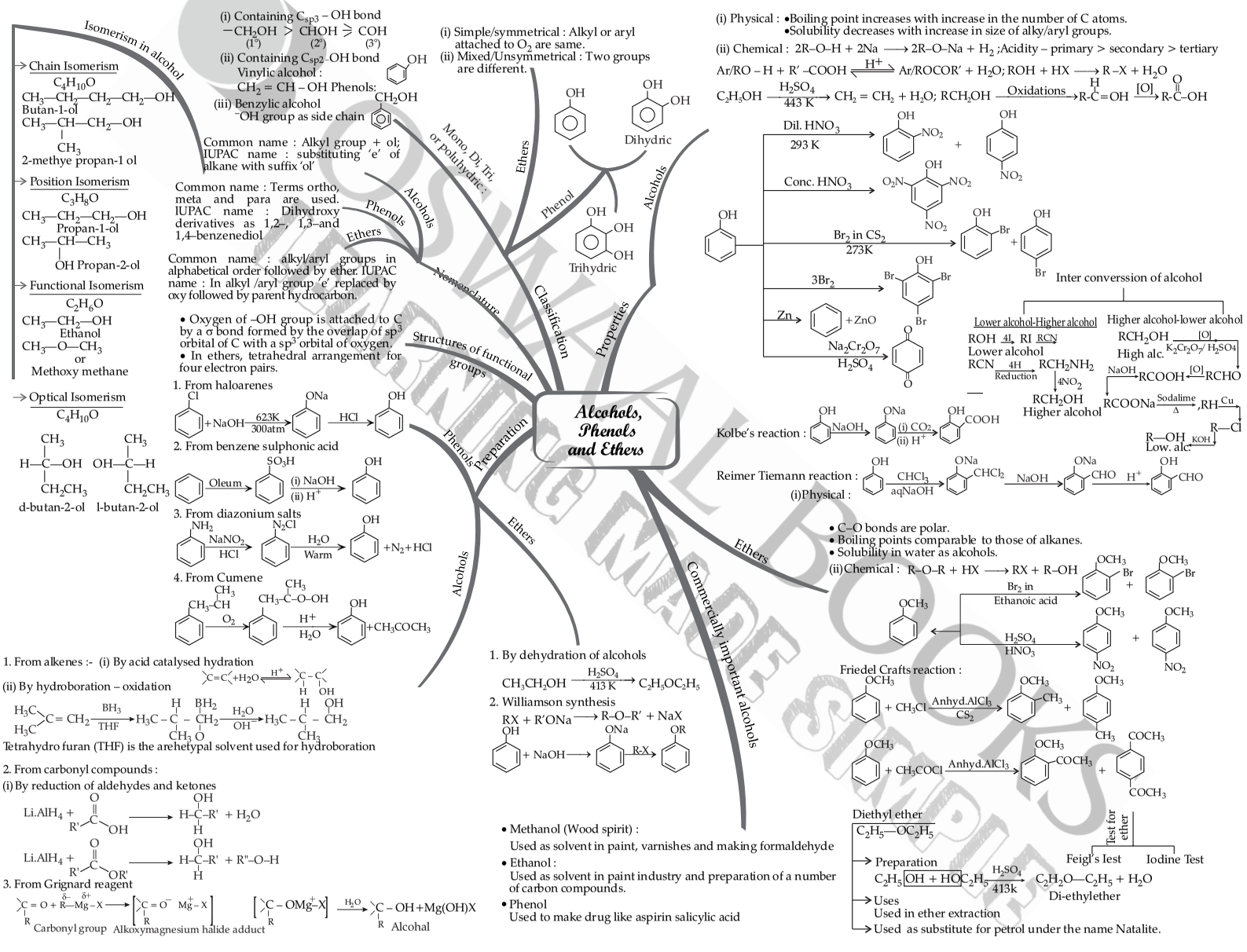
Polyhalogen compounds

- Antiseptic — Iodoform
- Carbon tetrachloride
- Freons
- D.D.T.
- As insecticide
- Dichloromethane

Racemisation S_N1

S_N2 Stereochemical inversion

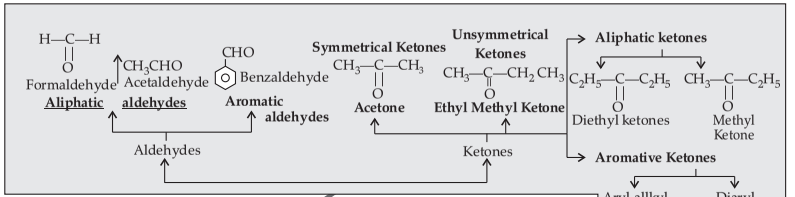
CHAPTER - 11 ALCOHOLS, PHENOLS AND ETHERS



CHAPTER - 12 ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Test	Aldehycle	Ketone
1. Tollen's reagent test	Give silver mirror	No action
2. Fehling's solution test	Give re Red ppt. (Benzaldehyde is an exception)	No action
3. Schiff reagent test	Restore pink colour	No action
4. Reaction with $LiAlH_4$	Form primary alcohols	Form secondary alcohols

Formaldehyde HCHO
Acetaldehyde CH_3CHO
Acetone $CH_3—CO—CH_3$
Benzaldehyde C_6H_5CHO



Aldehydes, Ketones and Carboxylic Acids

Properties

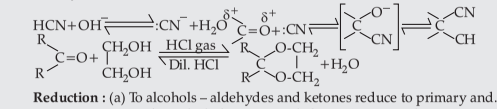
ALDEHYDES AND KETONES:

(i) Physical:

Boiling points are higher than hydrocarbons and ethers of comparable molecular masses.

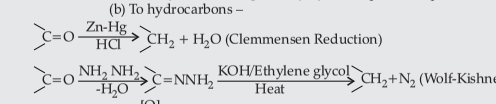
(ii) Chemical : Nucleophilic addition reactions :

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 –

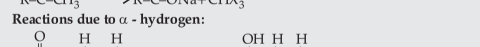


Oxidation: $RCHO \xrightarrow{[O]} R–COOH$

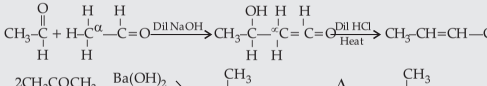
Tollen's test : $RCHO + 2[Ag(NH_3)]_2^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$

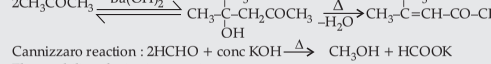
Fehling's test : $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$ (Red brown ppt)

Haloform reaction:



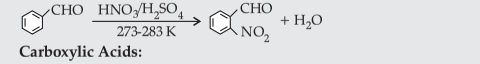
Reactions due to α - hydrogen:





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) Functional Derivatives of carboxylic acid

1) Acylhalide

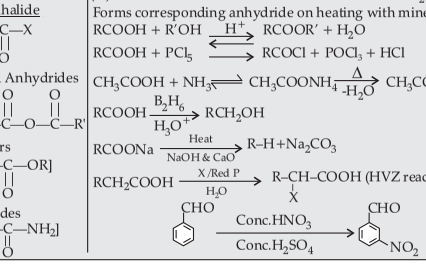
2) Acid Anhydrides

3) Esters

4) Amides

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

Forms corresponding anhydride on heating with mineral acids

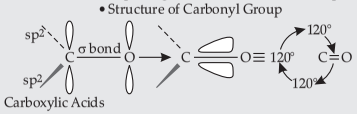


Distinguish b/w aldehydes & ketones

1. Aldehydes and Ketones

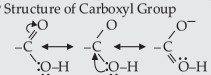
Common names :

- 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 tatty acids in manufacture of soaps and detergents.

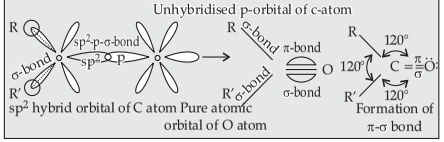
(b) Aldehydes of ketones

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

Structure of corbonyl group

- Carbon is in sp^2 hybridisation state
- C [Exicted state] $1s^2\ 2s^1\ 2px^1\ 2py^1\ 2pz^1$ (sp^2 hybridisation)

3 hybrid orbital of equal energy.



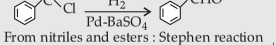
Commercially important aldehydes & ketones

Classification of aldehydes & ketones

Preparation

ALDEHYDES:

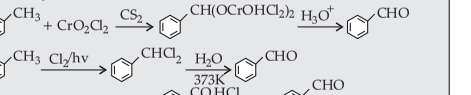
1. From acyl chloride



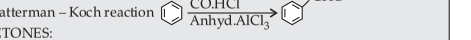
2. From nitriles and esters : Stephen reaction

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

3. From hydrocarbons : Etard reaction

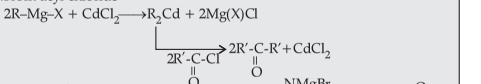


Gratterman – Koch reaction

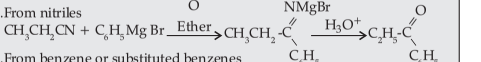


KETONES:

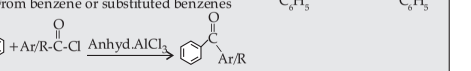
1.From acyl chloride



2.From nitriles



3.From benzene or substituted benzenes

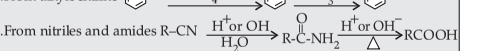


Carboxylic Acids:

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

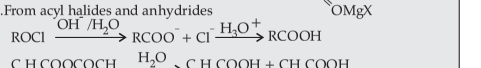
2.From alkylbenzine

3.From nitriles and amides R–CN

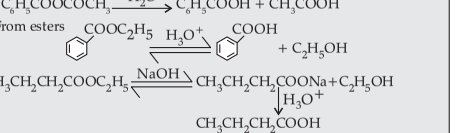


4.From Grignard reagents $R–Mg–X + CO_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-OMgX \xrightarrow{H_3O^+} RCOOH$

5.From acyl halides and anhydrides



6.From esters



Nomenclature

To know about more useful books for class-12 click here

CHAPTER - 13 ORGANIC COMPOUNDS CONTAINING NITROGEN

Organic Compounds Containing Nitrogen

Chemical reactions

(i) Basic character of amines

- Reacts with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- Reacts with base to regenerate parent amines $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $C_2H_5-NH(C_2H_5) + CH_3-CO-Cl \xrightarrow{Base} C_2H_5-N(C_2H_5)-CO-CH_3 + HCl$

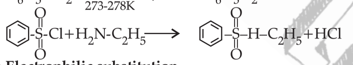
(iii) Carbylamines reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

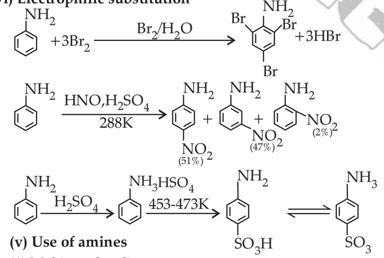
$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

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

(v) $C_6H_5-SO_2-Cl + H_2N-C_2H_5 \longrightarrow C_6H_5-SO_2-NH-C_2H_5 + HCl$



(vi) Electrophilic substitution



(v) Use of amines

(1) Making of aniline
(2) Quaternery salt derivatives are made

Test for amines 1°, 2°, 3° amines

(1) Solubility Test

(2) Carbylamine test $RNH_2 + CHCL_3 + KOH(ALE) \longrightarrow R-N=C + KEL + H_2O$ isocyamides

(3) Hisenberg test for distinguishing 1°,2°,3° amine Hisenberg reagent

Isomerism in amines

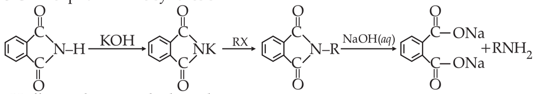
- Chain isomerism
  $C_4H_{11}N$: $CH_3-CH_2-CH_2-CH_2NH_2$ n- Butylamine
  $CH_3-CH(CH_3)-CH_2NH_2$ n- Isobutylamine
- Position isomerism
  C_3H_9N: $CH_3-CH_2-CH_2-CH_3$ 1-Aminepropane
  $CH_3-CH(NH_2)-CH_3$ 2-Aminepropane
- Metamerism
  $C_4H_{11}N$: $CH_3-CH_2-NH-CH_2CH_3$ Diethylamine
  $CH_3-CH_2-CH_2-NH-CH_3$ Methyl propylamine

More Compounds

- Ethylamine $C_2H_5NH_2$
- Aniline (Benzenuni) $C_6H_5NH_2$
- Test for amine :
  (1) Carbylamine test
  (2) Dye test

Preparation :

1. Reduction of nitro compounds: $C_6H_5NO_2 \xrightarrow[Ethanol]{H_2/Pd} C_6H_5NH_2$; $C_6H_5NO_2 \xrightarrow[or\ Fe+HCl]{Sn+HCl} C_6H_5NH_2$
2. Ammonolysis of alkyl halides: $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$
3. Reduction of nitriles: $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$
4. Reduction of amides: $R-CO-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$
5. Gabriel phthalimide synthesis



6. Hoffmann bromamide degradation reaction

$R-CO-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

Nitrocompounds

Structure $-NO_2$, $-N(=O)\rightarrow O$ or $\overset{+}{N}(=O)\rightarrow O^-$

Uses

- Nitromethane is used as solvent
- Nitroalkanes are used to make propellants
- Chloropicrin used to make insecticides

Nitrobenzene $C_6H_5NO_2$

- **Preparation :** Benzene $+ HNO_3 \xrightarrow[313\text{-}37\ K]{Conc.\ H_2SO_4}$ Nitrobenzene $+ H_2O$
- **Physical Properties :** Pale yellow oily liquid, steam volatile
- **Chemical Properties :**
  - Reduction: Nitrobenzene $\xrightarrow{2[H]}$ Nitrobenzene (No) $\xrightarrow{2[H]}$ N–Phenol hydeonyl amine (NHOH) $\xrightarrow[-H_2O]{2[H]}$ Amine (Nh_2)

Physical properties

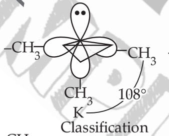
- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association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

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.

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

Structure



Classification

$NH_3 \rightarrow RNH_2 \rightarrow R(R')N-H \rightarrow R(R')N-R''$

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.

Cyanide and Isocyanides

$H-C\equiv N \rightleftharpoons H-N\equiv C$
Hydrogen Cyanide I — Hydrogen Cyanide II

Physical Properties : Colorless, crystalline, solids, High BP, fairly soluble

Preparation : $RX + \overset{+}{K}\overset{-}{C}N$ (alc.) $\xrightarrow{Heat} R-C\equiv N + \overset{+}{K} - \overset{-}{X}$

Chemical Properties :

- Hydrolysis $CH_3-C\equiv N \xrightarrow[HCL]{+H_2O} CH_3-CO-CH_3$ (Methyl Cyanide → Acetamide)
- Reduction $CH_3-C\equiv N + H_2 \xrightarrow[Pt]{Ni} CH_3CH_2NH_2$ Ethylamine

Uses : (i) Use to make ketone, aldehydes, acids

Diazonium Salts (RN_2X)

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

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

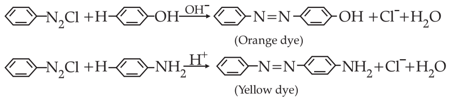
Chemical properties :

(i) Sandmeyer reaction: $ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$; $\xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$; $\xrightarrow{CuCN/KCN} ArCN + N_2$

Gattermann reaction :

$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$; $\xrightarrow{Cu/HBr} ArBr + N_2 + CuX$

(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$
(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$
(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$
(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$
(iv) **Coupling reaction :**



CHAPTER - 14 BIOMOLECULES

Biomolecules

Carbohydrates

On the basics of reduction behavior

Reducing Sugars : Reduce Tollen's reagent & fehlings solution.
Non Seducing Sugars : Do not reduce Tollen's reagent, fehlings solution.

On the basis of taste

Sugars
Non Sugars

Optically active polyhydroxy aldehydes or ketones or compounds which produce such units on hydrolysis.

TESTS

A. Test of glucose :
- Bromine water test. Color of Br disappears.
- Fehling solute test Red ppt of Cu_2O farmed.

B. Test for fructose :
- Bromine water test : Do not decolorise Br_2 water
- Furfural + alc α–nafthol + conc. HCL → Violet color

- **Classification:**

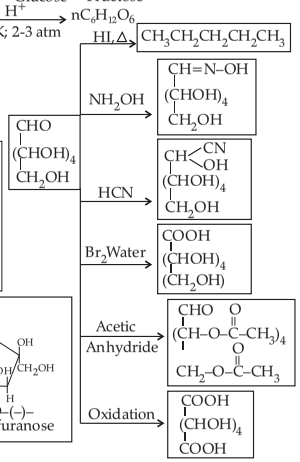
(I) Monosaccharides : (Aldehyde group – aldose, keto group –ketose)

Glucose : Preparation :

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

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

- **Structure:**



Oeigo Succharates

(ii) Disaccharides : Linkage between 2 monosaccharides– Glycosidic linkage (Sucrose, maltose)

(iii) Polysaccharides : Large number of monosaccharides units joined by glycosidic linkages.

(a) Starch : Polymer of α–glucose with two components amylase 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.

Proteins

Biological Importance
- As structural material
- As transport agent
- As calatyst
- As food reserve

(Polymers of α–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 –linke structure
  - (ii) Globular – spherical

Structure : $H_2N – CH_2 –$ CO–NH (Peptide linkage) $– CH(CH_3) – COOH$

Denaturation of proteins :
When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity by
- Heat
- Alcohol
- Radiation

Cellular energetics

Free energy charges in Biological reaction

$\Delta G = \Delta G_1 + \Delta G_2$

A ngatine quantity

Adenosine Triphosphate (ATP)
Energy packets in living organisms

Vitamins

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.

Hormones

Steroid Hormones:
- Peptide
- Hormone
- Amine hormones

DNA Fingerprinting:Unique sequence of bases on DNA

Enzymes

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

mechanism

Key & hock
- E + S → [ES]
- [ES] → [EP]
- EP → E + P

ES = Enzyme Substance
EP = Enzyme protein

Properties
- Specificity
- Calatylic efficiency
- Enzyme inhibition

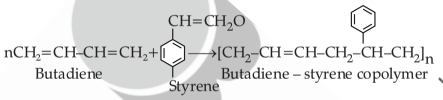
Some reactions
- Invertase : sucrose → Glucose + Fructose
- Amylase : Starch → nX Glucose
- Lactose : Lactose → Glucose + Galactose
- Urease: Urea → CO_2 + NH_3
- Pepsin : Protein → Amino acid
- Trypsin : Protein → Amino acid

CHAPTER - 15 POLYMERS

Polymers

Very large molecules having high molecular mass

Copolymerization : A mixture of more than one monomeric species undergoes polymerization



Rubber

Types :

(i) Natural rubber : natural and manufactured from rubber latex. It is a liner polymer of isoprene.

(ii) Synthetic rubber : Any vulcanisable rubber. These are homopolymers of 1,3 butadiene derivatives.

(iii) Nitrate Rubber : Buna-N
(iv) Butyl rubber : (G-R-I)
(v) Polysulphide rubber (Thiokol or GR-P)
(vi) Polyurethanes.

Molecular mass of polymers

- Expressed as an average.
- Determined by chemical and physical methods.

Biodegradable polymers

Contain functional groups similar to biopolymers (PHBV, Nylon 2–nylon 6)

Classification

Based on source of origin:

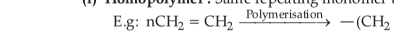
- **(i) Natural polymers :** Found in plants and animals. (Proteins, rubber)
- **(ii) Semi–synthetic polymers :** (Cellulose derivatives)
- **(iii) Synthetic polymers :** Man-made. (Polythene, Buna –S)

Based on structure of polymers high density:

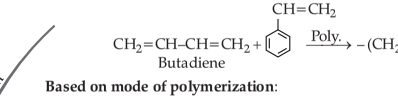
- **(i) Linear polymers :** Long and straight. (Polythene, PVC)
- **(ii) Branched chain polymers :** Linear chains with branches (low density polythene)
- **(iii) Cross linked or network polymers :** Strong covalent bond between various linear polymer chains. (Bakelite, Melamine)

Based on nature of repeating units

- **(i) Homopolymer :** Same repeating monomer units.



- **(ii) Copolymer :** repeating units are derived from two or More types of monomer units



Based on mode of polymerization:

- **(i) Addition polymers :** Repeated addition of monomers containing double or triple bonds. (Polythene from ethene)
  Homopolymer : Single monomeric species (Polythene)
  Copolymer : Two different monomers (Buna–S, Buna–N)
- **(ii) Condensation polymers :** Repeated condensation between two different bi–functional or tri–functional monomeric units. (Terylene, Nylon 6)

Based on Molecular Forces:

- **(i) Elastomers :** Rubber–like solids with elastic properties (Buna–S, Buna–N)
- **(ii) Fibres :** Thread forming solids. (Nylon 6,6, Terylene)
- **(iii) Thermoplastic polymers :** Linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling. (polythene, polystyrene)
- **(iv) Thermosetting polymers :** Cross linked or heavily branched molecules which on heating undergo extensive cross linking in moulds and become infusible. (Bakelite)

Commercially important polymers

(A) Polyolefin's
(1) Polyethena
(2) Polypropylene
(3) Polystyrene

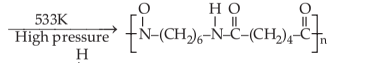
(B) Polydienes
(1) Neoprene
(2) Buna (s) Rubber

(C) Ployacrylates
(1) Polymethyl methacrylate (PMMA)
(2) Polyethyl acryclates
(3) Polyacrylonitrile

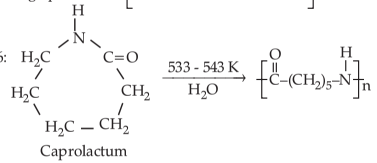
(D) Polyholo – Olefins
(1) Polytetra flouoro ethylene P(TFE)
(2) Polymono chloro trifluoro ethylene (PLTFE)
(3) Polyvinyl chlorides (PVC)

Preparation

- Polythene
  Low density : Polymerization of ethene under 1000–2000 atm at 350–570 K + catalyst
  Higher density : addition polymerization of ethene in a hydrocarbon solvent at 333–343 K and 6–7 atm + catalyst
- Teflon: $nCF_2 = CF_2 \xrightarrow[\text{High pressure}]{\text{Catalyst}} [CF_2–CF_2]_n$
- Polyacrylonitrile: $nCH_2=CHCN \xrightarrow[\text{Peroxide}]{\text{Polymerisation}} [CH_2–\underset{CN}{CH}]_n$
- Nylon 6,6: $nHOOC(CH_2)_4COOH + nH_2(CH_2)_6NH_2$

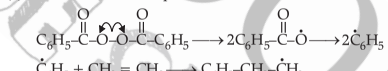


- Nylon 6:



Types of Polymerization Reactions

- (i) Addition/Chain Growth : Molecules of the same/different monomers add together on a large scale.
  Free radical mechanism :
  (a) Chain initiation step:



  (b) Chain propagating step:
  $C_6H_5–CH_2–\dot{C}H_2 + CH_2 = CH_2 \longrightarrow C_6H_5–CH_2–CH_2–CH_2–\dot{C}H_2 \longrightarrow C_6H_5–(CH_2–CH_2)n–CH_2–\dot{C}H_2$
  (c) Chain terminating step:
  $2[C_6H_5–(CH_2–CH_2)n–\dot{C}H_2–CH_2] \longrightarrow C_6H_5–(CH_2–CH_2)n–CH_2–CH_2 – CH_2–(CH_2 – CH_2)n–C_6H_5$
- (ii) Condensation/Step Growth : Repetitive condensation reaction between two bi–functional monomers. (Formation of terylene)

Condensation Polymers

(A) Polyesters :
- Terylene or Dacron
- Glyptal or Alkyl resin

(B) Polyamide :
- Nylon -66
- Nylon -610
- Nylon -6

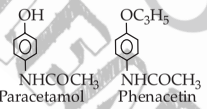
(C) Formaldehyde Resin :
- Phenol formaldehyde resin (Bakelite)
- Melamine – formaldehyde resin

CHAPTER - 16 CHEMISTRY IN EVERYDAY LIFE

Chemistry in Everyday Life

Therapeutic Action of Different Classes of Drugs

- **Antacids :** Substances that neutralize the excess HCl and raise pH in stomach (Ranitidine, Cimetidine)
- **Antihistamines :** Interfere with natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect
- **Neurologically Active Drugs**
  - (a) **Tranquilizers :** Class of chemical compounds used for the treatment of stress and mild or even severe mental diseases. (Iproniazid, Phenelzine)
  - (b) **Analgesics :** Reduce/abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or other disturbances of nervous system. These are classified as
    - (i) Non-narcotic (non-addictive) : (Aspirin, Paracetamol)
    - (ii) Narcotic : (Morphine)
- **Antipyretics**
  Chemical substances which are used to bring down body temperature at high fever



Paracetamol Phenacetin

- **Antimicrobials**
  - (a) Antibiotics : Drugs to treat infections because of their low toxicity for humans and animals. (Prontosil)
  - (b) Antiseptics and Disinfectants : Chemicals which either kill or prevent the growth of microorganisms. Antiseptics are applied to living tissues whereas disinfectants are applied to inanimate objects.
- **Antifertility Drugs :** Birth control pills (Norethindrone, ethynylestradiol)
- **Antibiotics**
  Produced lye certain micsorganam and destroy infections in human body.
  - Penicillin
  - Streptomycin

Chemicals In Food

Purpose:

- For their preservation.
- Enhancing their appeal.
- Adding nutritive value.
  - (a) Artificial Sweetening Agents : Natural sweeteners (sucrose), artificial sweeteners (Aspartame, Saccharin)
  - (b) Food Preservatives : Prevent spoilage of food due to microbial growth. (Table salt, sugar)

Antiseptics and Disinfectants

- Chlorine is used for purifying water
- Iodine is powerful antiseptic
- Deltol is an antiseptic
- Bithional is an antiseptic
- Boric acid in weak antiseptic for eyes

Chemicals in food

Saccharin, Atitame, Sucrolose → Flavors & sweetness

- Food colors
- Flavors & sweetness
- Antioxidants
- Preservatives
- For emulsifiers and stabilising agent

Cleansing Agents

Types: Detergents

(i) **Soap (Saponification)**

Glyceryl ester of stearic acid (fat) + Sodium hydroxide ⟶ Sodium stearate + Glycerol

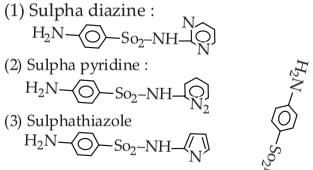
(ii) **Synthetic Detergents :**

- Anionic detergents : Sodium salts of sulphonated long chain alcohols or hydrocarbons. (sodium salts of alkyl benzene sulphonates)
- Cationic detergents : Quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. (Cetyltrimethylammonium bromide)
- Non-ionic Detergents : Non-ionic type.

Anionic detergents
Cationic detergents
Non conies detergents

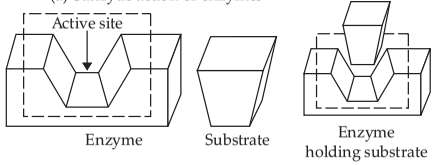
Sulpha Drugs

Some examples → Derivatives of Sulphanilamide

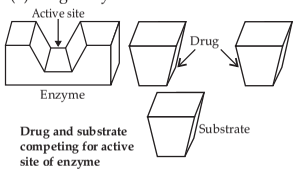


Medicines: Chemicals which generate therapeutic and useful biological response

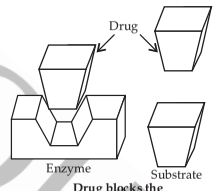
- Drugs are chemicals of low molecular masses. Interact with macromolecular targets to produce a biological response.
- **Classification of drugs:**
  - (a) On the basis of pharmalogical effect : Provides range of drugs available for a particular type of problem. (Analgesics, Antiseptics).
  - (b) On the basis of drugs action : (Antihistamines inhibit action of histamine responsible for causing inflammation in the body.
  - (c) On the basis of chemical structure : Common structural features. (Sulphonamides)
  - (d) On the basis of molecular targets : Most useful.
- **Drugs Target Interaction:**
  - (i) Enzymes as Drug Targets
    - (a) Catalytic action of enzymes



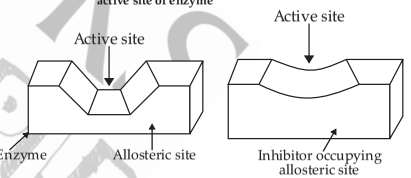
- (b) Drug–enzyme interaction



Drug and substrate competing for active site of enzyme



Drug blocks the active site of enzyme



(ii) **Receptors as Drug Targets**: Receptors are proteins crucial for body's communication and are embedded in cell membrane.