

- 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 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<sup>2+</sup>/M E°: E° for Mn, Ni and Zn are more negative than d-Block transition elements • Trends in M<sup>3+</sup>/M<sup>2+</sup> E°: variable • Chemical reactivity and E° values: Variable; Ti2+, V2+ and Cr2+ are strong reducing agents. • Magnetic properties: Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.  $\bullet$  Formation of coloured ions : Form coloured compounds due to d-d• Formation of complex compounds : Form a large number of complex • 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. Potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> Preparation:  $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$  $2Na_{2}CrO_{4} + 2H^{+} \rightarrow Na_{2}Cr_{2}O_{7} + 2Na^{+} + H_{2}O_{7}$  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ Properties:  $Cr_2 O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ Oxidises iodides to iodine, H<sub>2</sub>S to S, SO<sub>3</sub><sup>2-</sup> to SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup> to NO<sub>3</sub><sup>-</sup> Potassium permanganate KMnO<sub>4</sub> Preparation:  $2MnO_2 + 4KOH + O_2 \rightarrow 2KMnO_4 + 2H_2O$
- · Helps in production of iron and steels. • TiO in pigment industry • MnO2 in dry battery cells. • As catalysts in industry. • Ni complexes useful in the polymerization of
  - alkynes and other organic compounds such as benzene. Ag Br in photographic industry.

The d-And

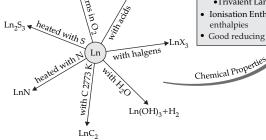
F- Block

Elements

- Electronic: configuration [Rn]5f<sup>1-14</sup> 6d<sup>0-2</sup>7s<sup>2</sup>
- 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.
- Electronic configuration  $4f^{1-14}\ 5d^{0-1}\ 6s^2$

Lanthanoids

- 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.

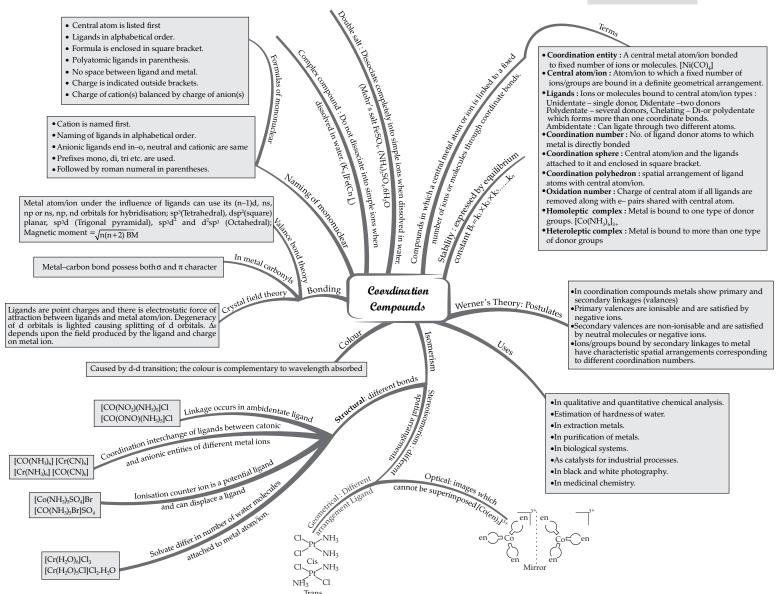


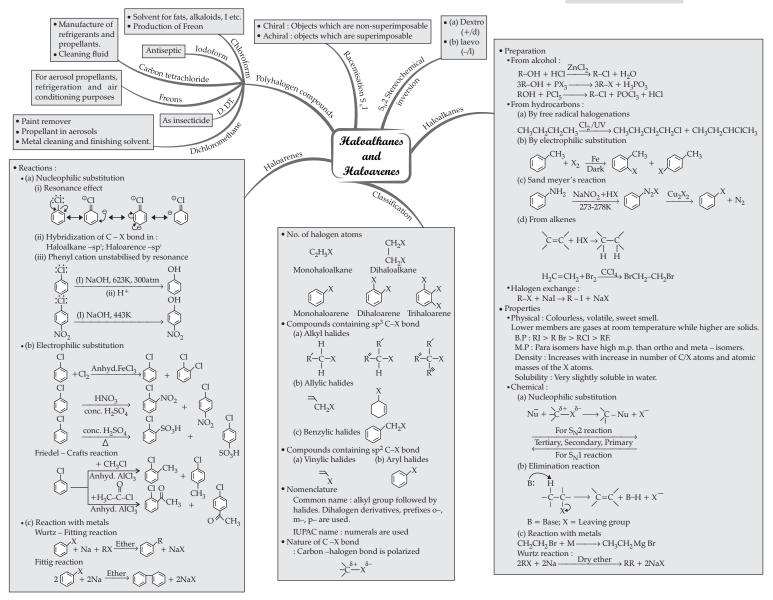
E. Block Transition Elements

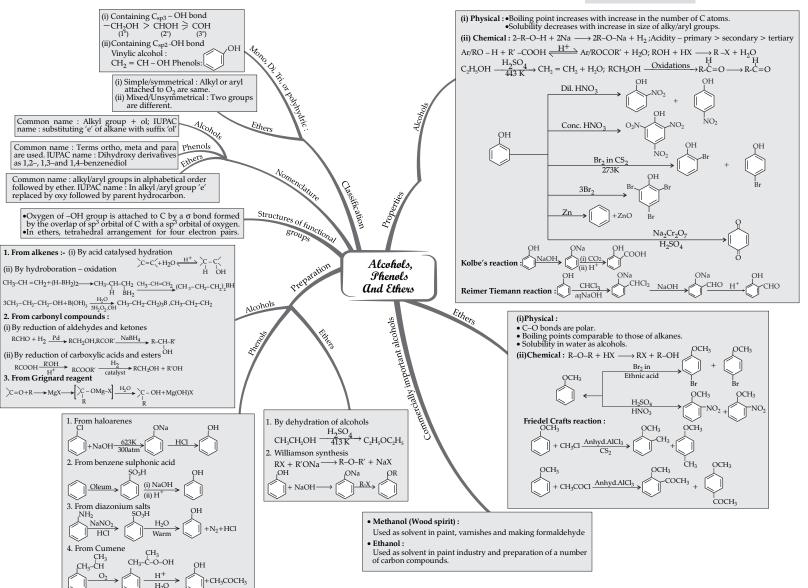
 $3 \text{ MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2 \text{ MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}^+$  $2Mn^{2+} + 5S_2O_3 + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$ Mn Properties: Intense colour, weak temperature dependent paramagnetism  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 

 $\circ$ 

Oxidizes I<sup>-</sup> to  $I_2$ ,  $Fe^{2+}$  to  $Fe^{3+}$ ,  $C_2 O_4^{2-}$  to  $CO_2$ ,  $S^{2-}$  to  $SO_2^{2-}$  to  $SO_4^{2-}$ , NO2 to NO3







### ALDEHYDES AND KETONES:

### (i) Physical:

Boiling points are higher than hydrocarbons and ethers of comparable

### (ii)Chemical:Nucleophilic addition reactions:

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

$$\begin{array}{c|c} HCN+OH \xrightarrow{\hspace*{-0.5cm}}: CN^- + H_2O \\ \hline R \\ C=O+ \begin{array}{c} CH_2OH \\ CH_2OH \end{array} \xrightarrow{\hspace*{-0.5cm}} \begin{array}{c} HCl \ gas \\ Dil. \ HCl \end{array} \xrightarrow{\hspace*{-0.5cm}} \begin{array}{c} \delta^+ \\ CO-CH_2 \\ R \end{array} \xrightarrow{\hspace*{-0.5cm}} \begin{array}{c} O^- \\ CN \end{array} \xrightarrow{\hspace*{-0.5cm}} \begin{array}{c} CN \\ CH \end{array}$$

Reduction: (a) To alcohols – aldehydes and ketones reduce to primary and. secondary alcohols respectively by NaBH<sub>4</sub> or LiAlH<sub>4</sub>. (b) To hydrocarbons -

$$C=O \xrightarrow{Zn-Hg} CH_2 + H_2O \text{ (Clemmensen Reduction)}$$

$$C=O \xrightarrow{NH_2 NH_2} C=NNH_2 \xrightarrow{KOH/Ethylene glycol} CH_2+N_2 \text{ (Wolf-Kishner)}$$

$$Heat$$

Oxidation: RCHO  $\xrightarrow{[O]}$  R-COOH Tollen's test: RCHO + 2[Ag(NH<sub>3</sub>)]<sub>2</sub> + 3OH $\xrightarrow{}$  RCOO $^-$  + 2Ag + 2H<sub>2</sub>O + 4NH<sub>3</sub> Fehling's test: RCHO + 2Cu<sup>2+</sup> + 5OH $\xrightarrow{}$  RCOO $^-$  + Cu<sub>2</sub>O + 3H<sub>2</sub>O

Haloform reaction:
$$\begin{array}{ccc}
O & O \\
R-C-CH_3 \xrightarrow{NaOX} R-C-ONa+CHX_3
\end{array}$$

## Reactions due to a - hydrogen:

Reactions due to 
$$\alpha$$
 - hydrogen: 
$$2\text{CH}_3\text{CHO} \xrightarrow{\text{diNaOH}} \text{CH}_3\text{-CH=CH-CHO} \xrightarrow{\Delta} \text{CH}_3\text{-CH=CH-CHO}$$

$$2\text{CH}_3\text{COCH}_3 \xrightarrow{\text{Ba(OH)}_2} \text{CH}_3 \xrightarrow{\text{C}} \text{CH}_3 \xrightarrow{\text{C}} \text{CH}_3 \xrightarrow{\Delta} \text{CH}_3 \xrightarrow{\text{C}} \text{C}} \xrightarrow{\text{C}} \text{CH}_3 \xrightarrow{\text{C}} \text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \text{C} \xrightarrow{\text{C}} \text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C}} \text{C}} \xrightarrow{\text{C}} \xrightarrow{\text{C$$

Cannizzaro reaction : 2HCHO + conc KOH  $\xrightarrow{\Delta}$  CH<sub>2</sub>OH + HCOOK Electrophilic substitution reaction:

$$\begin{array}{c}
C_2N \\
CHO \\
\hline
273-283 K
\end{array}$$
C<sub>2</sub>N CHO

### Carboxvlic acids:

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

Forms corresponding anhydride on heating with mineral acids RCOOH + R'OH  $\xrightarrow{H^+}$  RCOOK' + H<sub>2</sub>O RCOOH + PCl<sub>5</sub>  $\Rightarrow$  RCOCl + POCl<sub>3</sub> + HCl

$$RCOOH + PCI_5$$

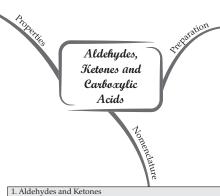
$$RCOCI + POCI_3 + HC$$

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2$$
B H

$$RCOOH \xrightarrow{H_3O^+} RCH_2OH$$

RCOONa 
$$\xrightarrow{\text{NaOH & CaO}}$$
 R-H+Na<sub>2</sub>CO<sub>3</sub>

RCOON a 
$$\frac{B_2H_6}{H_3O^4}$$
 RCH<sub>2</sub>OH  $\frac{B_2H_6}{H_3O^4}$  RCH<sub>2</sub>OH  $\frac{B_2H_6}{H_3O^4}$  RCH<sub>2</sub>COOH  $\frac{A \cdot R}{A \cdot A \cdot A \cdot A}$  R-CH-COOH (HVZ reaction)  $\frac{A \cdot R \cdot A}{A \cdot A \cdot A}$  CHO  $\frac{A \cdot R \cdot A}{A \cdot A \cdot A}$  CHO  $\frac{A \cdot R \cdot A}{A \cdot A}$  CHO  $\frac{A \cdot R \cdot A}{A}$  CHO  $\frac{$ 



### 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.

- . Carboxylic Acids
- Common names : end with -ic
- IUPAC names: replace -e in the corresponding alkane
- Structure of Carboxyl Group

(a) Carboxylic acids

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

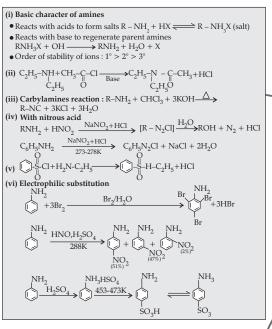
## (b) Aldehydes of ketones

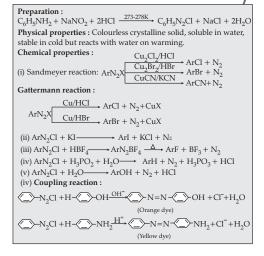
- As solvents.
- · Starting materials and reagents for synthesis of

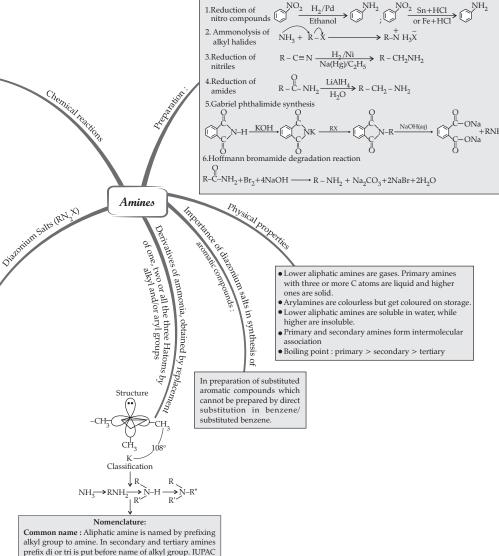
## ALDEHYDES: 1. From acyl chloride 2. From nitriles and esters: Stephen reaction $RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3O^+} R CHO$ 3. From hydrocarbons: Etard reaction $\bigcirc ^{\mathsf{CH}_3} + \mathsf{CrO}_2\mathsf{Cl}_2 \xrightarrow{\mathsf{CS}_2} \bigcirc ^{\mathsf{CH}(\mathsf{OCrOHCl}_2)_2} \xrightarrow{\mathsf{H}_3\mathsf{O}^+} \bigcirc ^{\mathsf{CHO}}$ Gratterman – Koch reaction $\bigcirc$ $\frac{\text{CO.HCl}}{\text{Anhyd.AlCl}_3}$ 1.From acyl chloride $2R-Mg-X + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$ $2R'\text{-C-Cl} \xrightarrow{2R'\text{-C-R'}+CdCl_2} 2R'\text{-C-R'}+CdCl_2$ 2.From nitriles $0 \qquad NMgBr$ $CH_3CH_2CN+C_9H_5MgBr\underline{Ether}CH_3CH_2-C'(\underline{H_3O^+}+C_9H_5-C')$ 3.From benzene or substituted benzenes 1.From primary alcohols and aldehydes $RCH_2OH \xrightarrow{Alk. KMnO_4} RCOOH$ 2.From alkylbenzine $\times$ KMnO<sub>4</sub>-KOH $\times$ COOK $\times$ COOH 3.From nitriles and amides R-CN $\xrightarrow{H^+ \text{or OH}}$ $\xrightarrow{H^+ \text{or OH}}$ $\xrightarrow{R^+ \text{c-NH}_2}$ $\xrightarrow{\Lambda}$ RCOOH 4.From Grignard reagents R-Mg-X + CO<sub>2</sub> $\longrightarrow$ R-O $\xrightarrow{\text{H}_3\text{O}^+}$ RCOOH $\xrightarrow{\text{OMgX}}$ 5.From acyl halides and anhydrides ROC1 $\xrightarrow{OH^{-}/H_{2}O}$ RCOO $^{-}$ + Cl $\xrightarrow{H_{3}O^{+}}$ RCOOH $C_1H_2COOCOCH_3 \xrightarrow{H_2O} C_2H_2COOH + CH_3COOH$ 6.From esters $COOC_2H_5 \xrightarrow{H_3O^+} COOH + C_2H_5OH$ $\mathsf{CH_3CH_2CH_2COOC_2H_5} \underbrace{\frac{\mathsf{NaOH} \setminus}{\mathsf{CH_3CH_2CH_2COONa} + \mathsf{C_2H_5OH}}}_{} \mathsf{CH_3CH_2CH_2COONa} + \mathsf{C_2H_5OH}$ CH,CH,CH,COOH

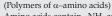
name: replacement of 'e' of alkane by the word amine.

Suffix 'e' of arene is replaced by amine.









Amino acids contain -NH2 and -COOH group.

### Classification:

- On the basis of relative number of -NH2 and -COOH group
  - (I) Neutral-equal number of -NH2 and -COOH group.
  - (ii) Basic more number of -NH2 than -COOH group.
  - (iii) Acidic more number of –COOH than –NH<sub>2</sub> 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

Peptide linkage

Structure: H<sub>2</sub>N - CH<sub>2</sub> - CO-NH - CH-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.

> Vitamins Biomolecules

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

- (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.

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  $\beta$ -D-2-deoxyribose whereas in RNA is  $\beta$ -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-Sugar-Phosphate-Sugar-

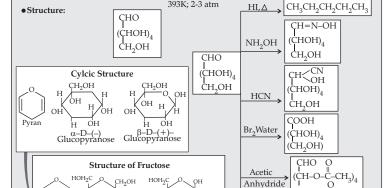
Types of RNA: m-RNA, r-RNA, t-RNA

## **Biological Functions:**

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

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

- Classification:
- (I) Monosaccharides: (Aldehyde group aldose, keto group –ketose) Glucose: Preparation:
- (a) From sucrose:  $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$
- Sucrose Slucose Fitzose (b) From starch :  $(C_6H_{10}O_5)n + nH_2O$   $H^+$   $nC_6H_{12}O_6$ 393K: 2-3 atm



- (ii) Disaccharides: Linkage between 2 monosaccharides- Glycosidic linkage (Sucrose, maltose)
- (iii) Polysaccharides: Large number of monosaccharides units joined by glycosidic linkages.

 $_{\rm H}$   $_{\rm OH}$   $_{\rm CH_2OH}$ 

он н

 $\beta$ -D-(-)-

fructofuranose

CH,-O-Ö-CH,

COOH

(CHOH),

COOH

Oxidation,

- (a) Starch: Polymer of α–glucose with two components amylase and amylopectin (b) Cellulose
- (c) Glycogen

DNA Fingerprinting:Unique sequence of  $b_{ases}$ 

### Importance:

- •Form a major portion of food.
- •As storage molecules.
- •Cellulose forms cell wall of bacteria and plants.

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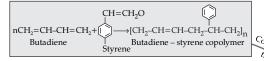
 $\alpha - D - (-) -$ 

fructofuranose

•Raw materials for industries like textiles, paper, lacquers and breweries.

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

**Polymers** 



### 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.

$$N-CH_2 = CI-CH = CH_2 \xrightarrow{Polymerisation} [CH_2-C=CH-CH_2]_n$$

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

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

Rubber

### · Based on source:

- (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 brankes (low density polythene)
  - (iii) Cross linked or network polymers: Strong covalent bond between various linear polymer chains. (Bakelite, Melamine)

### · 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)

## • 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: 
$$nCF_2 = CF_2 \xrightarrow{Catalyst} \{CF_2 - CF_2\}_n$$

- Polyacrylonitrile:  $nCH_2$ =CHCNPolymerisation
  Peroxide  $(CH_2-CH_1)$   $(CH_2-CH_2)$
- Nylon 6,6: nHOOC(CH<sub>2</sub>)<sub>4</sub> COOH + nH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>

• Nylon 6: 
$$H_{2}C$$
 $H_{2}C$ 
 $H_{$ 

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

- 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)

### 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)

## 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)

## Drugs are chemicals of low molecular masses. Interact with macromolecular targets to produce a biological response.

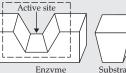
### • Classification of drugs:

- (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

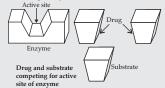
(a) Catalytic action of enzymes

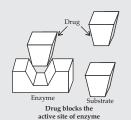


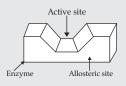


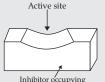
Substrate Enzyme holding substrate

(b)Drug-enzyme interaction









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

(i) Soap (Saponification)

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

## (ii) Synthetic Detergents:

 Anionic detergents: Sodium salts of sulphonated long chain alcohols or hydrocarbons. (sodium salts of alkyl benzene sulphonates)

Chemistry in Everyday Life

- Cationic detergents: Quaternary ammonium salts of amines with acetates, chlorides or bromides as anions. (Cetyltrimethylammonium bromide)
- Non-ionic Detergents : Non-ionic type.