Classification of Elements and Periodicity in Properties

Chapter 3

1 GENESIS OF PERIODIC CLASSIFICATION

- **Dobereiner's Triad:** Middle element of each of the triads had an atomic weight about half way between the atomic weights of other two and also the properties of middle element were in between other two.
  e.g. (Li, Na, K), (Ca, Sr, Ba), (Cl, Br, I)
- **Law of Octaves:** On arranging the elements increasing order of their atomic weights, every eighth element had properties similar to the first element e.g Li, Be, B, C etc resemble with Na, Mg ,Al and Si respectively.
- **Lother Meyer:** Plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained a periodically repeated pattern.
- **Mendeleev Periodic law:** The properties of elements are a periodic function of their atomic weights.
  Mendeleev predicted elements **Eka-Aluminium** as Gallium and **Eka-Silicon** as Germanium.

3 Nomenclature of elements having Z > 100

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name	IUPAC Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Un unnillium	Uun	Darmstadtium	Ds
111	Ununnunium	Uuu	Rontgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

2 MODERN PERIODIC LAW AND TABLE

- **Modern Periodic Law:** States that the physical and chemical properties of the elements are periodic functions of their atomic numbers.

- **Modern Periodic table**

PERIOD NUMBER	Representative elements GROUP NUMBER 1 (I A)	2 (II A)	d-Transition elements GROUP NUMBER 3 (III A)	4 (IV A)	5 (V A)	6 (VI A)	7 (VII A)	8 ← VIII →	9	10	11 (I B)	12 (II B)	Representative elements GROUP NUMBER 13 (III B)	14 (IV B)	15 (V B)	16 (VI B)	17 (VII B)	Noble gases 18 (0)
								1 H $1s^1$										2 He $1s^2$
1																		
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^1 4s^2$	22 Ti $3d^2 4s^2$	23 V $3d^3 4s^2$	24 Cr $3d^5 4s^1$	25 Mn $3d^5 4s^2$	26 Fe $3d^6 4s^2$	27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^1 5s^2$	40 Zr $4d^2 5s^2$	41 Nb $4d^4 5s^1$	42 Mo $4d^5 5s^1$	43 Tc $4d^5 5s^2$	44 Ru $4d^7 5s^1$	45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La * $5d^1 6s^2$	72 Hf $4f^{14} 5d^2 6s^2$	73 Ta $5d^3 6s^2$	74 W $5d^4 6s^2$	75 Re $5d^5 6s^2$	76 Os $5d^6 6s^2$	77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac ** $6d^1 7s^2$	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

f- Inner transition elements

*Lanthanoids $4f^n 5d^{0\text{-}1} 6s^2$	58 Ce $4f^2 5d^0 6s^2$	59 Pr $4f^3 5d^0 6s^2$	60 Nd $4f^4 5d^0 6s^2$	61 Pm $4f^5 5d^0 6s^2$	62 Sm $4f^6 5d^0 6s^2$	63 Eu $4f^7 5d^0 6s^2$	64 Gd $4f^7 5d^1 6s^2$	65 Tb $4f^9 5d^0 6s^2$	66 Dy $4f^{10} 5d^0 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
**Actinoids $5f^n 6d^{0\text{-}2} 7s^2$	90 Th $5f^0 6d^2 7s^2$	91 Pa $5f^2 6d^1 7s^2$	92 U $5f^3 6d^1 7s^2$	93 Np $5f^4 6d^1 7s^2$	94 Pu $5f^6 6d^0 7s^2$	95 Am $5f^7 6d^0 7s^2$	96 Cm $5f^7 6d^1 7s^2$	97 Bk $5f^9 6d^0 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

4 ELECTRONIC CONFIGURATION

- **3d series** from Z = 21 to Z = 30
- **4d series** from Z = 39 to Z = 48
- **4f-inner transition series** from Z = 58 to Z = 71, also known as **lanthanide series**
- **5f-inner transition series** from Z = 90 to Z = 103 also known as **actinoid series**

- General outer electronic configuration
  s-block = $ns^{1\text{-}2}$
  p-block = $ns^2 np^{1\text{-}6}$
  d-block = $(n-1)d^{1\text{-}10}\, ns^{0\text{-}2}$
  f-block = $(n-2)f^{1\text{-}14}(n-1)d^{0\text{-}1}ns^2$

5 IMPORTANT TERMINOLOGIES

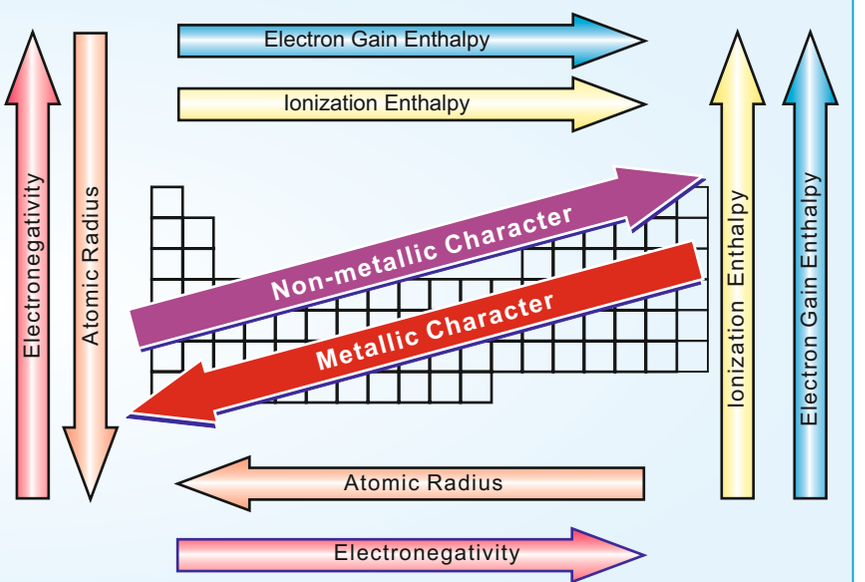
- **The elements of group 1 (alkali metals)** and **group 2 (alkaline earth metals)** are known as **s-block elements**.
- **The elements of group 13** to **18** are known as **p-block elements**.
- s-block and p-block elements together known as **Representative elements** or **Main Group elements**.
- All the orbitals in the valence shell of the **noble gases** are completely filled.
- **Group 17** elements are known as **halogens**.
- **Group 16** elements are known as **chalcogens**.
- Elements of **group 3** to **12** are known as **d-block elements**.
- **Transition metals** form a bridge between the **s-block elements** and **group 13 elements**
- Two rows of elements at the bottom of the periodic table called the **Lanthanoid** and **Actinoids** and combinely known as **Inner-transition elements** or **(f-block elements)**
- The elements after uranium are called **Transuranium elements**

6 PERIODIC TRENDS IN CHEMICAL PROPERTIES

- The **valence** of representative elements is usually equal to valence electrons or 8-valence electrons.
- Second period elements show **anomalous behaviour** due to their small size, large charge/radius ratio, high electronegativity of the elements and only four valence orbitals.
- Li and Be is more similar to Mg and Al respectively and this sort of similarity is known as **diagonal relationship**.
- The normal oxide formed by the element on extreme left is most **basic** (e.g. Na_2O), whereas that formed by the element on extreme right is most **acidic** (e.g. Cl_2O_7)
- Oxides of elements in centre are **amphoteric** (e.g. Al_2O_3, As_2O_3) or neutral (e.g. CO, NO, N_2O)
- **Amphoteric oxides** behaves as acidic with bases and as basic with acids, whereas neutral oxide have no acidic or basic properties.

7 TRENDS IN PHYSICAL PROPERTIES

- **Covalent radius** is half of the bond distance between two similar atoms.
- **Metallic radius** is half the inter nuclear distance separating the metal cores in the metallic crystal.
- **Atomic radius** refer to both covalent or metallic radius depending upon the element is a non metal or a metal
- Atoms or ions which contains same number of electrons are called **isoelectronic species** *e.g.* O^{2-}, F^-, Na^+ etc.
- **Ionic radii** can be estimated by measuring the distance between cations and anions
- A cation is always smaller than its parent atom while an anion is always bigger than its parent atom.
- **Ionization enthalpy** is the energy required to remove an electron from an isolated gaseous atom.
- Third ionization enthalpy is higher than second and so on.
- The effective nuclear charge experienced by a valence electron in an atom will be less than the actual charge on the nucleus because of the **"shielding"** or **"screening"** of valence electron from the nuclecus by intervening core electrons
- 2p electron of boron is more shielded from the nucleus than the 2s electron therefore ionization energy of boron is slightly less than that of beryllium.
- In nitrogen atom, three 2p-electrons reside in different orbitals whereas in oxygen atom, two of four 2p-electrons must occupy the same 2p-orbital resulting in increased repulsion therefore ionization enthalpy of N is greater than that of O.
- **Electron Gain enthalpy** is the enthalpy change when an electron is added to a gaseous neutral atom to convert it into a negative ion.
- Δ_{eg} H of O and F is less negative than that of succeeding element due to interelectronic repulsion.
- **Electronegativity** is a qualitative measure of the ability of an atom in a chemical bond to attract shared electrons.
- F is the most electronegative element while the electron gain enthalpy of Cl is most negative.



Sharpen Your Understanding

1. Incorrect Dobereiner's triad among the following is [NCERT Pg. 75]
(1) Li, Na and K (2) Ca, Sr and Ba
(3) Cl, Br and I (4) C, N and O

2. On the basis of Mendeleev, the properties of the elements are a periodic function of their [NCERT Pg. 76]
(1) Atomic number
(2) Atomic weight
(3) Number of neutron
(4) Number of electrons

3. Eka-aluminium is [NCERT Pg. 76]
(1) B (2) Si
(3) Ga (4) Ge

4. Atomic number of the element having syombal Uno is [NCERT Pg. 80]
(1) 108 (2) 107
(3) 105 (4) 102

5. Element having atomic number 29 belongs to [NCERT Pg. 87]
(1) 3d series
(2) 4d series
(3) 4f inner transition series
(4) 5f inner transition series

6. General outer electronic configuration of d-block elements is [NCERT Pg. 84]
(1) $nd^{1-10}(n-1)s^{0-2}$ (2) $(n-1)d^{1-10}ns^{0-2}$
(3) $nd^{1-10}(n-1)s^{2}$ (4) $(n-1)d^{10}ns^{0-2}$

7. Minimum ionic radii among the following is of [NCERT Pg. 87]
(1) Na^{+} (2) Mg^{2+}
(3) Al^{3+} (4) F^{-}

8. Correct order of first ionization enthalpies is [NCERT Pg. 88]
(1) Li <Be<B<C (2) Li <B<Be<C
(3) Li <C<Be<B (4) Li <B<C<Be

9. Maximum negative electron gain enthalpy among the following is of [NCERT Pg.90]
(1) F (2) O
(3) N (4) Cl

10. On Pauling scale, electronegativity of C is similar to [NCERT Pg. 91]
(1) S (2) Si
(3) P (4) N

11. Valence of group 15 elements is [NCERT Pg.92]
(1) 1 (2) 3
(3) 5 (4) Both (2) and (3)

12. Maximum covalency of Al is [NCERT Pg. 94]
(1) 1 (2) 3
(3) 6 (4) 8

13. Amphoteric oxide among the following is [NCERT Pg.94]
(1) Al_2O_3 (2) N_2O
(3) Na_2O (4) CO_2

14. N^{3-} and Na^{+} ions have same [NCERT Pg. 96]
(1) Atomic number
(2) Mass number
(3) Number of electrons
(4) Same number of neutorns

NCERT Based MCQs

15. Element having atomic number 15 belongs to [NCERT Pg. 97]
(1) 15^{th} group, 2^{nd} period
(2) 15^{th} group, 3^{rd} period
(3) 13^{th} group, 2^{nd} period
(4) 13^{th} group, 3^{rd} period

16. If Δ_iH_1 and Δ_iH_2 of an element are 419 and 3051 kJ mol^{-1} respectively then element belongs to [NCERT Pg. 98]
(1) 1^{st} group (2) 2^{nd} group
(3) 13^{th} group (4) 15^{th} group

17. Which of the following metal is a typical d-block element? [NCERT Pg.84]
(1) Zn (2) Cr
(3) Cd (4) Hg

18. 4^{th} period of periodic table contains [NCERT Pg.81]
(1) 8 elements (2) 18 elements
(3) 32 elements (4) 58 elements

19. Minimum negative electron gain enthalpy among the following is of [NCERT Pg.90]
(1) O (2) S
(3) Se (4) Te

20. Which of the following property generally increases down the group? [NCERT Pg.91]
(1) Atomic radius
(2) Ionization enthalpy
(3) Electronegativity
(4) Electron gain enthalpy

Thinking in Context

1. According to Law of octaves, on arranging the elements in increasing order of their atomic weights, every _____ element had properties similar to the first element. [NCERT Pg. 75]
2. According to Modern periodic law, the physical and chemical properties of elements are periodic functions of their _____. [NCERT Pg. 78]
3. 16^{th} group elements also known as _____. [NCERT Pg. 84]
4. Size of anion is always _____ than its parent atom. [NCERT Pg. 87]
5. Maximum covalency of first member of each group is _____. [NCERT Pg. 93]
6. Second ionization enthalpy will be _____ than the first ionization enthalpy. [NCERT Pg. 88]
7. Elements which show properties that are characteristic of both metals and non-metals are called _____. [NCERT Pg. 85]
8. Plot of 1^{st} ionization enthalpy vs atomic number, the minima occur at the _____. [NCERT Pg. 88]
9. Be is diagonally related to _____ . [NCERT Pg. 93]
10. d-block metals are _____ electropositive than group 1 and 2 metals. [NCERT Pg. 95]
11. Half of the internuclear distance separating the metal cores in the metallic crystal is know as _____. [NCERT Pg. 88]
12. s and p-block elements together are also known as _____. [NCERT Pg. 84]
13. Element having electronic configuration $[Rn]5f^{14}6d^{10}7s^{2}7p^{5}$ belongs to _____ period. [NCERT Pg. 84]
14. Hydrogen resembles with both _____ and _____. [NCERT Pg. 82]
15. 5f inner transition series is also known as _____ series. [NCERT Pg. 82]
16. Atomic radius generally _____ across a period from left to right. [NCERT Pg. 86]
17. Radii of noble gases should be compared with _____ radii of other elements. [NCERT Pg. 86]
18. Second electron gain enthalpy of oxygen atom is _____. [NCERT Pg. 90]
19. Elements in the same group have similar _____ properties. [NCERT Pg. 96]
20. Element having maximum chemical reactivity in terms of oxidising property is _____. [NCERT Pg. 99]

❑ ❑ ❑

Organic Chemistry - Some Basic Principles and Techniques

Chapter 12

1 CLASSIFICATION OF ORGANIC COMPOUNDS

Organic Compounds

- Acyclic or open chain
- Cyclic or closed chain
  - Alicyclic compounds
    - Homocyclic or carbocyclic compounds
    - Heterocyclic compounds (non-aromatic)
  - Aromatic compounds
    - Benzenoid compounds
    - Non-benzenoid compounds
    - Heterocyclic aromatic compounds

2 NOMENCLATURE

Abbreviation for alkyl groups

$CH_3-CH(CH_3)-$ Isopropyl –

$CH_3-CH_2-CH(CH_3)-$ sec-Butyl –

$(CH_3)_2CH-CH_2-$ Isobutyl –

$(CH_3)_3C-$ tert-Butyl –

$CH_3-C(CH_3)_2-CH_2-$ Neopentyl –

Nomenclature of Branched Chain Alkanes: (Rules)

(a) Longest carbon chain is identified

(b) Numbering is done so that branched carbon atoms get the lowest possible numbers

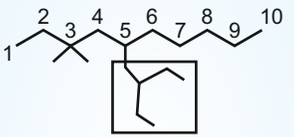
(c) For two substituents present at equivalent positions, the lower number is given to the one coming first in alphabetical listing

(d) For branched alkyl groups, the carbon atom of the branch that attaches to the root alkane is numbered (1) such as

$^{4}CH_3-\underset{CH_3}{^{3}CH}-^{2}CH_2-\underset{CH_3}{^{1}CH}-$ (1, 3-Dimethylbutyl) –

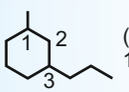
(e) While writing the names of the substituents in alphabetical order, the prefixes iso and neo are considered to be the part of fundamental name of alkyl group but sec- and tert- are not considered to be the part of fundamental name.

(f) If two chains are of equal size then that chain is to be selected which contains more number of side chains



5-(2-Ethylbutyl)-3, 3-dimethyldecane

Nomenclature of Cyclic Compounds



(Alphabetic order of numbering)
1-Methyl-3-propylcyclohexane

Nomenclature of organic compounds having functional groups(s)

(a) The functional group present in the molecule is identified which determines the choice of appropriate suffix.

(b) The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.

(c) The order of decreasing priority for some functional groups:

$-COOH, -SO_3H, -COOR, -COCl, -CONH_2, -CN,$

$-HC=O, \quad C=O, \quad -OH, \quad -NH_2, \quad C=C, \quad -C\equiv C-$

$^{6}CH_3-\overset{O}{\overset{\|}{^{5}C}}-^{4}CH_2-^{3}CH_2-\overset{O}{\overset{\|}{^{2}C}}-^{1}CH_3$

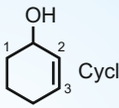
Hexane-2, 4-dione

$^{6}CH_3-\overset{O}{\overset{\|}{^{5}C}}-^{4}CH_2-^{3}CH_2-^{2}CH_2-^{1}COOH$

5-Oxohexanoic acid

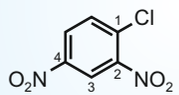
$^{5}CH_2=^{4}CH-^{3}CH_2-\underset{OH}{^{2}CH}-^{1}CH_3$

Pent-4-en-2-ol

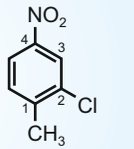


Cyclohex-2-en-1-ol

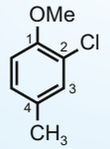
Nomenclature of substituted benzene compounds



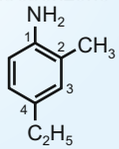
1-Chloro-2, 4-dinitrobenzene



2-Chloro-1-methyl -4-nitrobenzene



2-Chloro-4-methylanisole



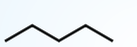
4-Ethyl-2-methylaniline

3 ISOMERISM

(a) **Structural Isomerism**

Compounds having the same molecular formula but different structures are classified as structural isomers.

(i) **Chain isomerism:** Example, C_5H_{12} represents three chain isomers

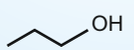


Pentane

2-Methylbutane

(2, 2-Dimethylpropane)

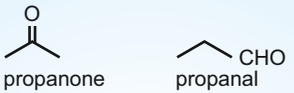
(ii) **Position isomerism:** Example, C_3H_8O represents two alcohols



Propan-1-ol

Propan-2-ol

(iii) **Functional group isomerism:** Example, C_3H_6O represents an aldehyde and a ketone



propanone propanal

(iv) **Metamerism:**

It arises due to different alkyl chains on either side of the functional group.

Example : $CH_3OC_3H_7$ and $C_2H_5OC_2H_5$ are metamers.

(b) **Stereoisomerism**

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. They are classified as

(i) Geometrical isomerism

(ii) Optical isomerism

4 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM

Organic molecule (Substrate) $\xrightarrow{\text{Attacking reagent}}$ [Intermediate] $\rightarrow$ Byproduct(s)

$\downarrow$

Product(s)

(a) **Fission of Covalent bond**

(i) **Heterolytic cleavage** and (ii) **Homolytic cleavage**

(i) **Heterolytic cleavage**

In heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

- **Carbocations:**
  - A species having a carbon atom possessing sextet of electrons and a positive charge is called carbocation.
  - Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects.
    - Stability order:

$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

- **Carbanions:**
  - A carbon species carrying a negative charge on carbon atom is called carbanion.
  - Carbon in carbanion is generally sp^3 hybridised and its structure is distorted tetrahedral.
    - Stability order:

$\bar{C}H_3 > CH_3\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(ii) **Homolytic cleavage:** One of the electrons of the shared pair in a covalent bond goes with each of bonded atoms resulting in formation of free radicals.

- Free radicals : Stability order

$\dot{C}H_3 < CH_3\dot{C}H_2 < (CH_3)_2\dot{C}H < (CH_3)_3\dot{C}$

(b) **Nucleophiles and Electrophiles**

- **Nucleophiles:** A reagent that brings an electron pair to the reactive site is called a nucleophile (Nu:)

Examples: H_2O, NH_3, $CH_3\bar{O}$, $\bar{S}H$

- **Electrophile :** A reagent that takes away an electron pair from reactive site is called electrophile (E^+)

Example: $AlCl_3$, BF_3, $\overset{+}{N}O_2$, Cl^+

(c) **Electron Displacement Effects in Covalent Bonds**

(i) **Inductive effect**

- When covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom.
- It operates through σ-bonds
- The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom.
- It is a permanent effect
- It is of two types

+I effect : e.g. $-CH_3$, $-CH_2CH_3$ etc.

–I effect : e.g. $-NO_2$, –CN, –CHO, –COOH etc.

(ii) **Resonance structures**

- Benzene can be represented by energetically identical structures (I) and (II) called resonance structures.

(I) (II)

- Actual structure is resonance hybrid of (I) and (II)
- The resonance structures (canonical structures) are hypothetical and individually do not represent any real molecule.
- The energy of actual structure of the molecule is lower than that of any of the canonical structures.
- The difference in energy between the actual structure and the lowest energy resonance structure is called the resonance energy.

(iii) **Resonance effect**

- It is a permanent effect
- It operates through π-bond(s)
- It is of two types

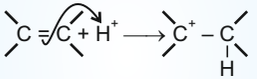
+R effect : Halogens, –OH, –OR, –OCOR, $-NH_2$ etc.

–R effect : –COOH, –CHO, –CN, $-NO_2$ etc.

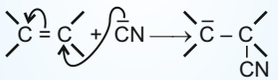
(iv) **Electromeric effect**

- It is a temporary effect
- Organic compounds having multiple bond (a double or triple bond) show this effect in presence of attacking reagent
- It is of two types

Positive electromeric effect (+E effect)

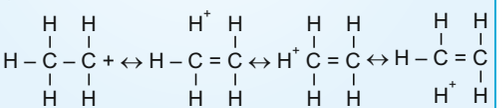


Negative electromeric effect (–E effect)



(v) **Hyperconjugation**

- It involves delocalisation of σ electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared *p* orbital



- It is a permanent effect.

5 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

The common techniques used for purification:

(i) Sublimation (ii) Crystallisation

(iii) Distillation : It is used to separate

(a) Volatile liquids from non-volatile impurities.

(b) The liquids having sufficient difference in boiling points e.g. mixture of chloroform (b.p. 334 K) and aniline (b.p. 457 K) is separated by this method.

(c) Distillation can be achieved by three different ways

- **Fractional Distillation:** This is applicable if boiling points of two liquids is not much, e.g. this is applicable to separate different fractions of crude oil in petroleum industry.

- **Steam Distillation:** This technique is applied to separate substances which are steam volatile and are immiscible with water.
  Example: Aniline is separated by this technique from aniline water mixture.
- **Distillation under reduced pressure:** This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points.
  Example: Glycerol can be separated from spent-lye in soap industry by using this technique.

(iv) **Differential Extraction:**

- When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- The organic solvent and the aqueous solution should be immiscible with each other.
- They form distinct layer which can be separated by separatory funnel.
- The compound is obtained by evaporating the organic solvent.

(v) **Chromatography:** It is an important technique extensively used to separate mixtures into their components.
Based on the principle involved it is classified into two main categories.

(a) Adsorption chromatography and
(b) Partition chromatography

(a) **Adsorption Chromatography:** It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. It is of two types
- Column chromatography
- Thin layer chromatography

(b) **Partition Chromatography:** It is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

6 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test. The elements present in the compound are converted from covalent form into the ionic form by fusing compound with sodium metal.

$Na + C + N \xrightarrow{\Delta} NaCN$

$2Na + S \xrightarrow{\Delta} Na_2S$; $Na + X \xrightarrow{\Delta} NaX$ (X = Cl, Br or I)

(A) **Test for nitrogen**

$6\bar{C}N + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$

$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{x H_2O} \underset{\text{(Prussian blue)}}{Fe_4[Fe(CN)_6]_3 \cdot xH_2O}$

(B) **Test of Sulphur**

(i) $S^{2-} + Pb^{2+} \rightarrow$ **PbS (black)**

(ii) $S^{2-} + \underset{\text{Nitroprusside}}{[Fe(CN)_5NO]^{2-}} \rightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$

In case, nitrogen and sulphur both are present, sodium thiocyanate is formed

$Na + C + N + S \rightarrow NaSCN$

$Fe^{3+} + S\bar{C}N \rightarrow [Fe(SCN)]^{2+}$ **(Blood red)**

(C) **Test of Halogen**

$X^- + Ag^+ \rightarrow AgX$

- A white precipitate, soluble in NH_4OH shows presence of chlorine.
- A yellowish precipitate soluble, sparingly soluble in NH_4OH shows presence of Br
- A yellow precipitate insoluble in NH_4OH shows presence of iodine

(D) **Test of Phosphorus**

$$\text{Compound} \xrightarrow{Na_2O_2} Na_3PO_4 \xrightarrow{HNO_3} H_3PO_4$$
$$\underset{\text{(Yellow ppt)}}{(NH_4)_3PO_4 \cdot 12\,MoO_3} \xleftarrow{(NH_4)_2\,MoO_4} \text{(from } H_3PO_4\text{)}$$

7 QUANTITATIVE ANALYSIS

(A) **Nitrogen is estimated by Dumas and Kjeldahl's method**

(i) **Dumas method**

Let volume of nitrogen at STP = V mL
Mass of organic compound = m g

$$\text{Percentage of nitrogen} = \frac{28 \times V \times 100}{22400 \times m}$$

(ii) **Kjeldahl's Method**

$$\text{Organic compound} + H_2SO_4 \rightarrow (NH_4)_2SO_4 \xrightarrow{NaOH} NH_3 \xrightarrow{H_2SO_4} (NH_4)_2SO_4$$

Let mass of organic compound = m g
Volume of H_2SO_4 of molarity M needed for neutralisation of ammonia produced = V mL

$$\% \text{ of nitrogen} = \frac{V \times 2M \times 1.4}{m}$$

- Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in ring (e.g. pyridine).

(B) **Halogens**

Carius method:

$$\text{Organic compound} \xrightarrow[AgNO_3\,\Delta]{\text{Fuming } HNO_3} AgX \downarrow$$

Let mass of compound = m g
Mass of AgX formed = m_1 g

$$\% \text{ of halogen} = \frac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of Ag X} \times m} \%$$

(C) **Sulphur**

Carius method:

$$\text{Organic compound} \xrightarrow{Na_2O_2} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 \downarrow$$

Let mass of compound = m g
Mass of $BaSO_4$ = m_1 g

$$\% \text{ of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m} \%$$

(D) **Phosphorus**

$$\text{Organic compound} \xrightarrow[HNO_3]{\text{Fuming}} H_3PO_4 \xrightarrow{(NH_4)_2MoO_4} (NH_4)_3PO_4 \cdot 12MoO_3 \downarrow$$

Let mass of compound = m g
Mass of $(NH_4)_3PO_4 \cdot 12MoO_3$ = m_1 g
Molar mass of $(NH_4)_3PO_4 \cdot 12MoO_3$ = 1877 g

$$\% \text{ of P} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$

Sharpen Your Understanding

1. Number of σ and π bonds present in the given molecule respectively are

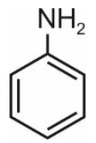
$CH_3 - CH = CH - CH = CH - CN$

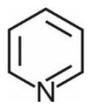
[NCERT Pg. 335]

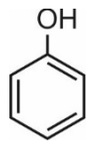
(1) 13 and 3 (2) 13 and 2

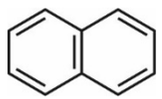
(3) 14 and 4 (4) 13 and 4

2. Which among the following is heterocyclic aromatic compound? [NCERT Pg. 340]

(1) 

(2) 

(3) 

(4) 

3. Isobutyl group among the following is [NCERT Pg. 341]

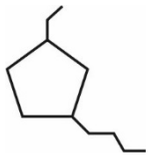
(1) $CH_3-CH_2-CH(CH_3)-$

(2) $CH_3-CH(CH_3)-CH_2-$

(3) $CH_3-C(CH_3)_2-$

(4) $CH_3 - CH_2 - CH_2 - CH_2 -$

4. IUPAC name of the given compound is



[NCERT Pg. 343]

(1) 1-Butyl-3-ethylcyclopentane

(2) 3-Butyl-1-ethylcyclopentane

(3) 1-Butyl-4-ethylcyclopentane

(4) 4-Butyl-1-ethylcyclopentane

5. Propanone and propanal are

[NCERT Pg. 349]

(1) Chain isomers

(2) Metamers

(3) Position isomers

(4) Functional group isomers

6. Most stable carbocation among the following is [NCERT Pg. 349]

(1) $Ph-\overset{\oplus}{C}H_2$ (2) $(CH_3)_3\overset{+}{C}$

(3) $(CH_3)_2\overset{+}{C}H$ (4) $CH_3\overset{+}{C}H_2$

7. Consider the following statements.

[NCERT Pg. 351]

(a) A reagent that takes away an electron pair is called an electrophile

(b) A nucleophile is electron rich species

(c) In methyl halide, carbon is electrophilic centre

Correct statements are

(1) (a) and (b) only (2) (b) and (c) only

(3) (a), (b) and (c) (4) (a) and (c) only

8. Which among the following is a temporary effect? [NCERT Pg. 355]

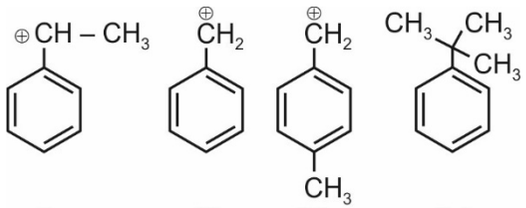
(1) Hyperconjugation

(2) Resonance

(3) Inductive effect

(4) Electromeric effect

9. Consider the following species



(i) (ii) (iii) (iv)

[NCERT Pg. 355]

Hyperconjugation will be observed in

(1) (i) and (ii) only

(2) (ii) and (iii) only

(3) (i) and (iii) only

(4) (i), (ii), (iii) and (iv)

10. The group which shows –I and –R effect is [NCERT Pg. 352, 354]

(1) –Cl (2) –OR

(3) $-NO_2$ (4) –NHCOR

NCERT Based MCQs

11. Mixture of aniline and chloroform can be easily separated by [NCERT Pg. 357]

(1) Distillation

(2) Fractional distillation

(3) Steam distillation

(4) Sublimation

12. On treating sodium fusion extract with sodium nitroprusside solution blood red colour is obtained. It indicates the presence of which element(s) in the organic compound? [NCERT Pg. 363]

(1) Nitrogen only

(2) Sulphur only

(3) Phosphorous only

(4) Nitrogen and sulphur both

13. Most stable carbanion among the following is [NCERT Pg. 350]

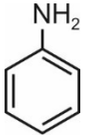
(1) $\overset{\ominus}{C}H_2-NO_2$

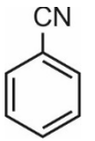
(2) $\overset{\ominus}{C}H_3$

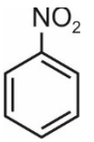
(3) $(CH_3)_2\overset{\ominus}{C}H$

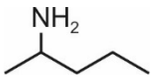
(4) $\overset{\ominus}{C}H_2-Ph$

14. Kjeldahl's method is not applicable to which compound? [NCERT Pg. 366]

(1) 

(2) 

(3) 

(4) 

15. In sulphur estimation 0.25 g of an organic compound gave 0.466 g of barium sulphate. Percentage of sulphur in the compound is [NCERT Pg. 367]

(1) 45.5%

(2) 16.4%

(3) 56.5%

(4) 25.6%

16. The element which cannot be detected by Lassaigne's test is [NCERT Pg. 362]

(1) Nitrogen

(2) Sulphur

(3) Chlorine

(4) Oxygen

17. Commonly used adsorbent(s) in column chromatography is/are [NCERT Pg. 360]

(1) Silica gel

(2) Alumina

(3) Charcoal

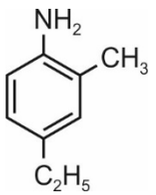
(4) Both (1) and (2)

18. Which among the following is a nucleophile? [NCERT Pg. 351]

(1) BF_3 (2) B_2H_6

(3) $\overline{S}H$ (4) $AlCl_3$

19. IUPAC name of the given compound is



[NCERT Pg. 347]

(1) 4-Ethyl-2-methylaniline

(2) 4-Amino-1-ethyl-3-methylbenzene

(3) 4-Ethyl-6-methylaniline

(4) 4-Amino-1-ethyl-5-methylbenzene

20. Which among the following is a planar molecule? [NCERT Pg. 335]

(1) $CH_2 = CH - CN$

(2) $CH_2 = C = CH_2$

(3) $CH_3 - CH = CH_2$

(4) $CH_3 - CH = CH - CH_3$

Thinking in Context

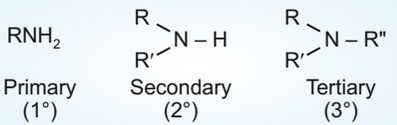
1. Urea can be synthesised by heating _____. [NCERT Pg. 334]
2. _____ arises due to different alkyl chains on either side of the functional group. [NCERT Pg. 349]
3. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to _____ and _____ effects. [NCERT Pg. 349]
4. A reagent that takes away an electron pair is called _____. [NCERT Pg. 351]
5. The _____ structures are hypothetical and individually do not represent any real molecule. [NCERT Pg. 353]
6. The IUPAC group prefix 'formyl' is used for _____. [NCERT Pg. 345]
7. _____ structures have same number of unpaired electrons. [NCERT Pg. 353]
8. _____ is also termed as no bond resonance. [NCERT Pg. 356]
9. In _____ cleavage, radical formation takes place. [NCERT Pg. 349]
10. _____ technique is applied to separate substances which are steam volatile and are immiscible with water. [NCERT Pg. 359]
11. Paper chromatography is a type of _____ chromatography. [NCERT Pg. 362]
12. The sodium fusion extract is boiled with ferrous sulphate and then acidified with concentrated sulphuric acid, formation of Prussian blue colour confirms the presence of _____. [NCERT Pg. 363]
13. Nitrogen, sulphur, halogens and _____ present in an organic compound are detected by Lassaigne's test. [NCERT Pg. 362]
14. Ammonium phosphomolybdate is _____ coloured compound. [NCERT Pg. 363]
15. In quantitative estimation of halogens by Carius method, a known mass of organic compound is heated with fuming nitric acid in presence of _____ in Carius tube. [NCERT Pg. 367]
16. Hyperconjugation involves delocalization of σ electrons of C – H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared _____. [NCERT Pg. 355]
17. Methyl propanoate and butanoic acid are _____. [NCERT Pg. 348]
18. The structural unit _____ is called neopentyl group. [NCERT Pg. 341]
19. Glycerol is separated from spent-lye in soap industry by using _____ technique. [NCERT Pg. 358]
20. $[Fe(SCN)]^{2+}$ is _____ in colour. [NCERT Pg. 363]

❑ ❑ ❑

Amines

Chapter 13

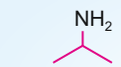
1 CLASSIFICATION



Primary (1°) | Secondary (2°) | Tertiary (3°)

- Amines are said to be simple when all the alkyl groups are same and mixed when they are different.

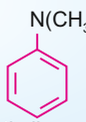
2 NOMENCLATURE



Propan-2-amine

$CH_3 - NH - CH_2CH_3$
N-methylethanamine

Propan-2-en-1-amine



N,N-Dimethylbenzenamine

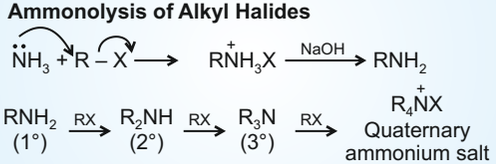
3 PREPARATION OF AMINES

(i) Reduction of nitro compounds

a. $PhNO_2 \xrightarrow[\text{Ethanol}]{H_2/Pd} PhNH_2$

b. $PhNO_2 \xrightarrow[\text{or Fe + HCl}]{Sn/HCl} PhNH_2$

(ii) Ammonolysis of Alkyl Halides



- Ammonolysis has disadvantage of yielding a mixture of primary, secondary, tertiary amines and also quaternary ammonium salt
- Primary amine is obtained as major product by taking large excess of NH_3.

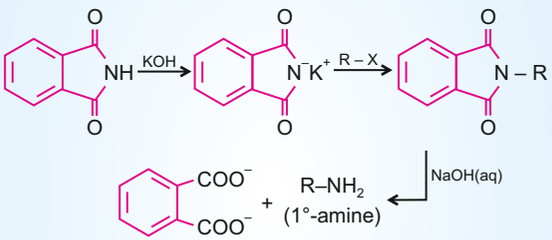
(iii) Reduction of Nitrites

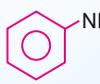
$$R-CN \xrightarrow[\text{or } H_2/Ni \text{ or } Na(Hg)/C_2H_5OH]{LiAlH_4} R-CH_2-NH_2$$

(iv) Reduction of amides

$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

(v) Gabriel phthalimide Synthesis



- This method is useful in the preparation of aliphatic primary amine
- Aromatic primary amine  is not prepared by this method because arylhalide donot undergo nucleophilic substitution reaction.

(vi) Hoffmann bromamide degradation reaction

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

- Primary amine formed contains one carbon less than that present in the amide.

4 PHYSICAL PROPERTIES

- Aniline and other arylamines are usually colourless but get colour on storage due to atmospheric oxidation
- Lower aliphatic amines are soluble in water because they form hydrogen bonds with water molecules.
- Order of boiling points of isomeric amines: Primary > Secondary > Tertiary

5 CHEMICAL REACTIONS

(i) Basic character of amines

- Order of bascity of amines in gaseous phase:

  tertiary amine > secondary amine > primary amine > NH_3
- Basic nature of amines in aqueous medium:

  (a) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

  (b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- Aryl amines are less basic than alkylamines because in arylamine the lone pair on nitrogen is involved in resonance.

(ii) Alkylation

$$R-NH_2 + CH_3-Br \longrightarrow RNH-CH_3 + HBr$$

(iii) Acylation

$$C_2H_5\ddot{N}H_2 + CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{Base} C_2H_5-NH-\overset{\overset{O}{\|}}{C}-CH_3 + HCl$$

(iv) Carbylamine reaction (chemical test)

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

It is used as a test for primary amines

(v) Reaction with nitrous acid (With primary aliphatic amine)

$$R-NH_2 + HNO_2 \xrightarrow[HCl]{NaNO_2} [R-\overset{\oplus}{N_2}Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$$

(vi) Reaction with arylsulphonyl chloride (Hinsberg's reagent)

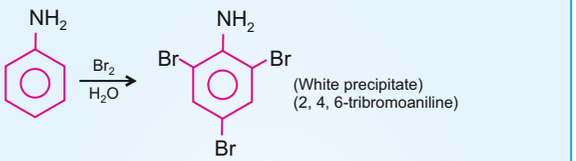
- Reaction with primary amine

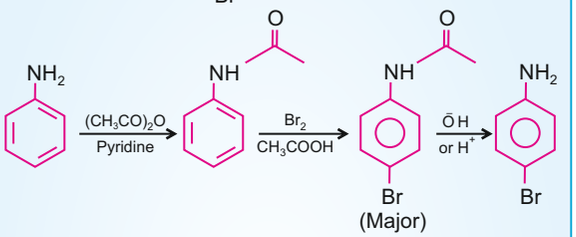
  $PhSO_2Cl + C_2H_5\ddot{N}H_2 \longrightarrow PhSO_2NHC_2H_5$ (Soluble in alkali)
- Reaction with secondary amine

  $PhSO_2Cl + (C_2H_5)_2\ddot{N}H \longrightarrow PhSO_2N(C_2H_5)_2$ (insoluble in alkali)
- Tertiary amines do not react with benzensulphonyl chlorides.

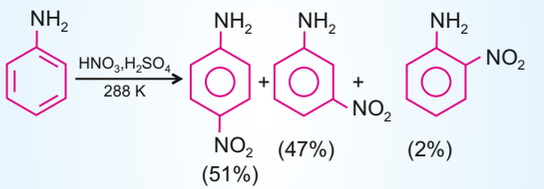
(vii) Electrophilic substitution reaction:

(a) Bromination

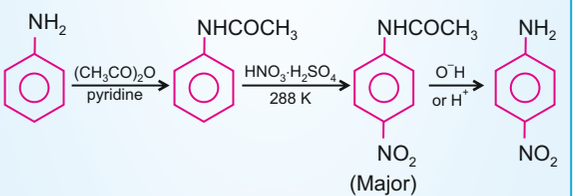




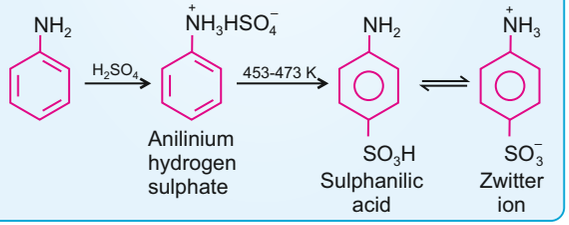
(b) Nitration



- Controlled nitration reaction

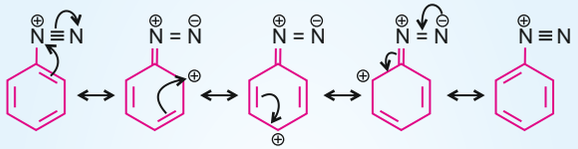


(c) Sulphonation



6 DIAZONIUM SALTS

- Primary aliphatic amines form highly unstable alkyldiazonium salts.
- Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperature (273-278 K) due to resonance



(i) Method of preparation of $C_6H_5\overset{\oplus}{N}_2\overset{\ominus}{Cl}$

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278\ K} C_6H_5\overset{\oplus}{N}_2\overset{\ominus}{Cl} + NaCl + 2H_2O$$

(ii) Physical properties

- Benzenediazonium chloride is colourless crystalline solid and readily soluble in water.
- It is stable in cold but reacts with water when warmed.
- Benzenediazonium Fluoroborate is water insoluble and stable at room temperature.

(iii) Chemical reactions

A. Reactions involving displacement of nitrogen

(a) Replacement by halide or cyanide ion

Sandmeyer reaction

$$ArN_2^+X^- \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$$
$$ArN_2^+X^- \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$$
$$ArN_2^+X^- \xrightarrow{CuCN/KCN} ArCN + N_2$$

Gatterman reaction

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

(b) Replacement by iodide ion

$$ArN_2^+Cl^- + KI \rightarrow ArI + KCl + N_2$$

(c) Replacement by fluoride ion

$$ArN_2^+Cl^- + HBF_4 \rightarrow ArN_2^+BF_4^- \xrightarrow{\Delta} Ar - F + BF_3 + N_2$$

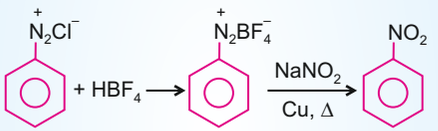
(d) Replacement by Hydrogen

$$ArN_2^+Cl^- + H_3PO_2 + H_2O \rightarrow ArH + N_2 + H_3PO_3 + HCl$$
$$ArN_2^+Cl^- + CH_3CH_2OH \rightarrow ArH + N_2 + CH_3CHO + HCl$$

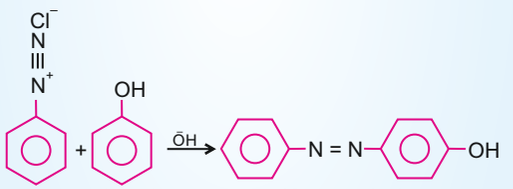
(e) Replacement by hydroxyl group

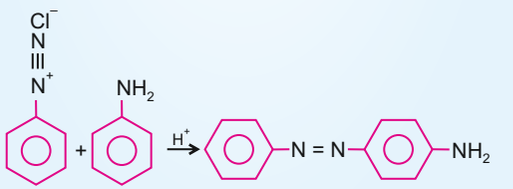
$$ArN_2^+Cl^- + H_2O \xrightarrow{283\ K} ArOH + N_2 + HCl$$

(f) Replacement by $-NO_2$ group



B. Reactions involving retenation of diazo group (Coupling reaction)





Sharpen Your Understanding

1. Consider the following amines

[NCERT Pg. 396]

$C_2H_5N(CH_3)_2$ (i) $(C_2H_5)_2NH$ (ii) $n-C_4H_9NH_2$ (iii)

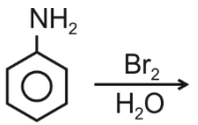
the correct order of their boiling points is

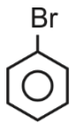
(1) (ii) > (i) > (iii) (2) (iii) > (ii) > (i)

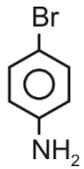
(3) (i) > (ii) > (iii) (4) (ii) > (iii) > (i)

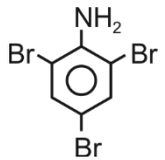
2. Major product of the given reaction is

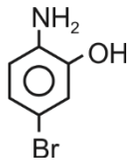
[NCERT Pg. 402]



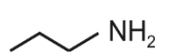
(1) 

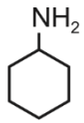
(2) 

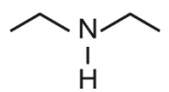
(3) 

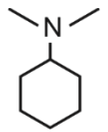
(4) 

3. The amine which will not react with Hinsberg's reagent is [NCERT Pg. 401]

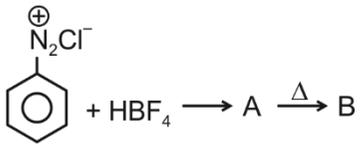
(1) 

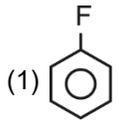
(2) 

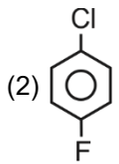
(3) 

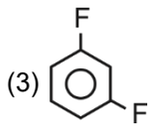
(4) 

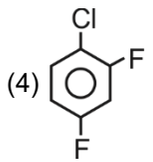
4. In the given reaction sequence major product B is [NCERT Pg. 405]



(1) 

(2) 

(3) 

(4) 

5. Incorrect statement among the following is

[NCERT Pg. 390, 393, 397, 401]

(1) Amines are said to be simple when all alkyl or aryl groups are same

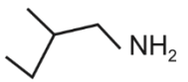
(2) Benzyl amine is more basic than aniline

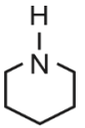
(3) Alkyl nitriles are reduced to primary amine by $LiAlH_4$

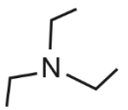
(4) Aliphatic diazonium salts are more stable than aromatic diazonium salts at low temperature

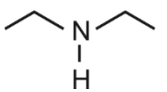
6. Which compound on reaction with chloroform and ethanolic potassium hydroxide form isocyanide?

[NCERT Pg. 401]

(1) 

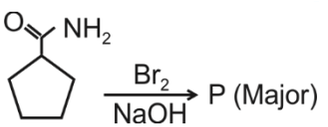
(2) 

(3) 

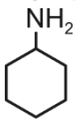
(4) 

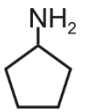
7. Consider the following reaction

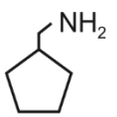
[NCERT Pg. 394]

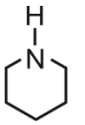


Major product P is

(1) 

(2) 

(3) 

(4) 

8. Correct order of basic strength of given compounds in aqueous medium is

[NCERT Pg. 399]

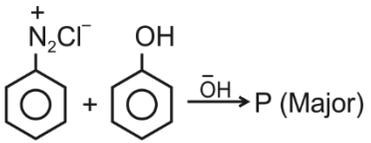
$(C_2H_5)_3N$ (a) NH_3 (b) $(C_2H_5)_2NH$ (c) $C_2H_5NH_2$ (d)

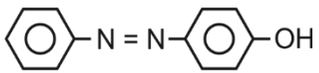
(1) (a)>(c)>(d)>(b) (2) (c)>(b)>(a)>(d)

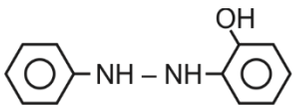
(3) (c)>(a)>(d)>(b) (4) (c)>(d)>(a)>(b)

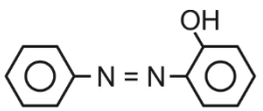
9. In the given reaction major product P is

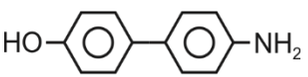
[NCERT Pg. 406]



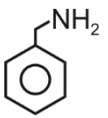
(1) 

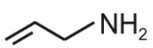
(2) 

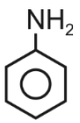
(3) 

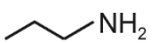
(4) 

10. Which among the following compounds cannot be prepared by Gabriel phthalimide synthesis? [NCERT Pg. 394]

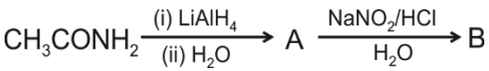
(1) 

(2) 

(3) 

(4) 

11. Consider the given set of reactions



Major product B is [NCERT Pg. 393, 401]

(1) CH_3COOH

(2) CH_3CH_2OH

(3) CH_3CH_2Cl

(4) $CH_3CH_2NO_2$

12. When benzene diazonium chloride is treated with ethanol then the product obtained is [NCERT Pg. 405]

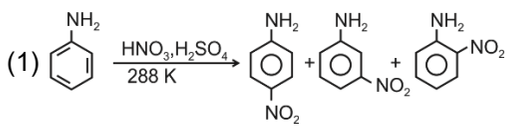
(1) Aniline

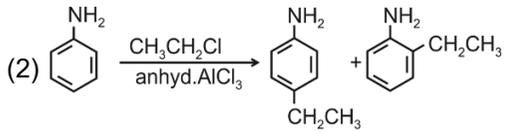
(2) Phenetole

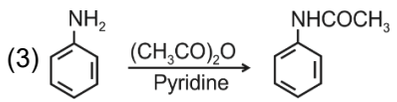
(3) Benzene

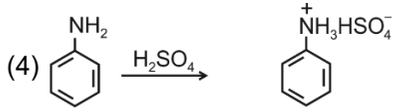
(4) p-chlorophenol

13. Which of the following reaction does not occur? [NCERT Pg. 403]

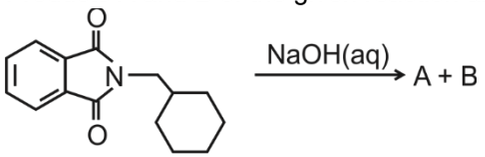
(1) 

(2) 

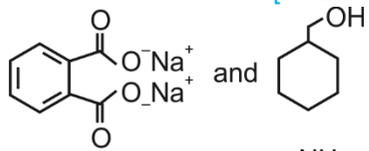
(3) 

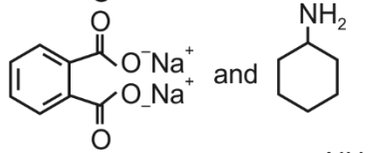
(4) 

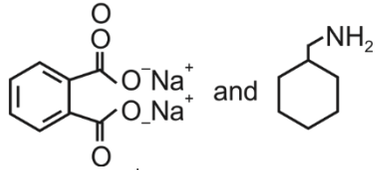
14. Products A and B of the given reaction are

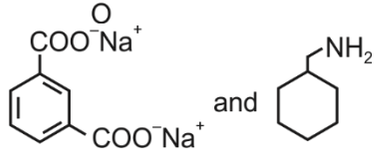


[NCERT Pg. 394]

(1) 

(2) 

(3) 

(4) 

15. Consider the following statements

(a) Hoffman bromamide degradation reaction is used for the preparation of secondary amines.

(b) Benzenediazonium fluoroborate is readily soluble in water.

(c) In Gattermann reaction, diazonium salt solution is treated with corresponding halogen acid in presence of copper powder.

The correct statement(s) is/are [NCERT Pg. 394, 405]

(1) (a) and (b) only (2) (b) and (c) only

(3) (c) only (4) (b) only

16. Aniline and N-methylaniline can be chemically distinguished by [NCERT Pg. 401]

(1) $CHCl_3|KOH|\Delta$

(2) Aqueous H_2SO_4

(3) Aqueous NaOH

(4) CH_3COCl/pyridine

17. Hinsberg's reagent is [NCERT Pg. 401]

(1) $SOCl_2$ (2) $C_6H_5SO_2Cl$

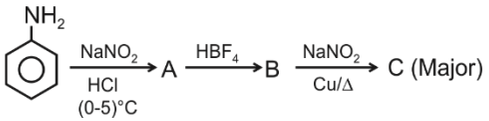
(3) C_6H_5COCl (4) $NaNO_2/HCl$

18. The amine which is most basic in gas phase is [NCERT Pg. 398]

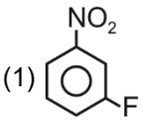
(1) CH_3NH_2 (2) NH_3

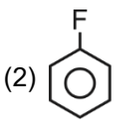
(3) $(CH_3)_2NH$ (4) $(CH_3)_3N$

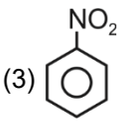
19. Consider the following reaction sequence

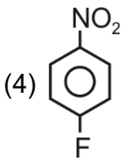


Product C is [NCERT Pg. 404, 406]

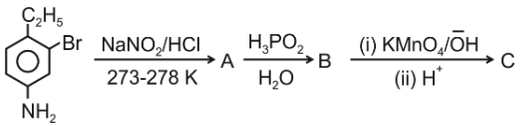
(1) 

(2) 

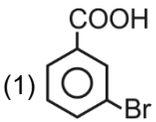
(3) 

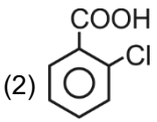
(4) 

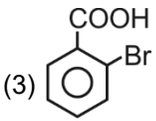
20. Product C of the given reaction sequence is

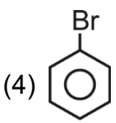


[NCERT Pg. 407]

(1) 

(2) 

(3) 

(4) 

Thinking in Context

1. IUPAC name of $C_2H_5 - \underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{N}} - CH_2 - CH_2 - CH_2 - CH_3$ is _____. [NCERT Pg. 391]

2. Nitrobenzene is reduced to _____ in presence of Sn/HCl. [NCERT Pg. 392]

3. Number of resonating structures in aniline is _____. [NCERT Pg. 399]

4. _____ reacts with acetyl chloride in presence of base giving N, N-diethylethanamide. [NCERT Pg. 400]

5. Carbylamine reaction is a chemical test of _____ amines. [NCERT Pg. 401]

6. Aliphatic diazonium salts in aqueous medium liberate _____ gas quantitatively and _____. [NCERT Pg. 401]

7. _____ reacts with primary and secondary amines to form sulphonamide. [NCERT Pg. 401]

8. _____ amines do not react with benzene sulphonyl chloride [NCERT Pg. 402]

9. Activating effect of-$NHCOCH_3$ group is _____ than that of $-NH_2$ group [NCERT Pg. 403]

10. Structure of sulphanilic acid is _____. [NCERT Pg. 403]

11. Aniline does not undergo Friedel-Crafts reaction due to salt formation with _____. [NCERT Pg. 403]

12. Benzenediazonium chloride is _____ in water. [NCERT Pg. 405]

13. The conversion of primary aromatic amines into diazonium salts is known as _____. [NCERT Pg. 404]

14. When diazonium salt solution is treated with _____, iodobenzene is formed. [NCERT Pg. 405]

15. Ethanol reduces diazonium salts to arenes and itself get oxidised to _____.
[NCERT Pg. 405]

16. If the temperature of diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to _____. [NCERT Pg. 406]

17. p-aminoazobenzene is _____ colour dye
[NCERT Pg. 406]

18. Coupling reaction of diazonium salt with aniline yields p-aminoazobenzene is an example of _____ reaction.
[NCERT Pg. 406]

19. In strongly acidic medium, aniline is protonated to form anilinium ion which is _____ directing towards electrophilic substitution reaction. [NCERT Pg. 403]

20. Basic nature of aniline is _____ than that of ammonia. [NCERT Pg. 399]

❑ ❑ ❑

Biomolecules

14 Chapter

1 CARBOHYDRATES

Classification of Carbohydrates:

A. Monosaccharides: A carbohydrate that cannot be hydrolysed further to give simpler unit of polyhydroxy aldehyde or ketone. Examples: Glucose, fructose, arabinose etc.

B. Oligosaccharides: These carbohydrates yield two to ten monosaccharide units on hydrolysis. They are further classified as disaccharides, trisaccharides etc.

C. Polysaccharides: They yield a large number of monosaccharide units on hydrolysis.

Example : Starch, Cellulose etc.

Monosaccharides:

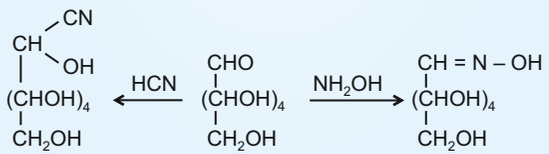
- If a monosaccharide contains an aldehyde group, it is known as an aldose and if contains a keto group, it is called ketose

(a) Glucose: It is an aldohexose

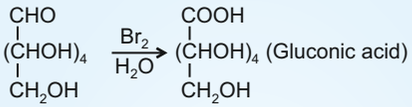
Structure of glucose

Glucose has been assigned the structure $CHO-(CHOH)_4-CH_2OH$ on the basis of following evidences:

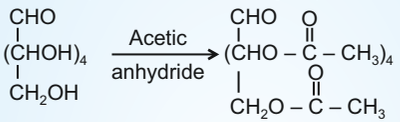
- Its molecular formula is found to be $C_6H_{12}O_6$.
- On prolonged heating with HI, it forms n-hexane, suggesting carbons are linked in straight chain.
- Presence of carbonyl group is confirmed by the following reactions.



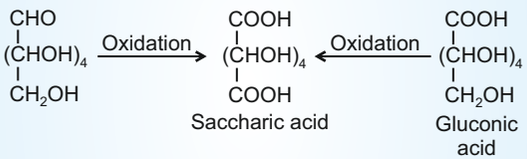
- Carbonyl group present is an **aldehyde** is confirmed by the given reaction



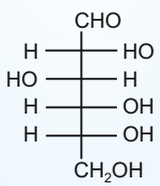
- Acetylation of glucose gives glucose pentaacetate which confirms presence of five OH groups



- Glucose and gluconic acid is oxidised to saccharic acid by nitric acid. This indicates presence of primary –OH group

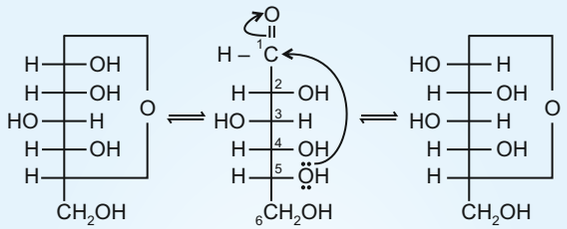


- Fischer suggested following configuration of D(+) glucose

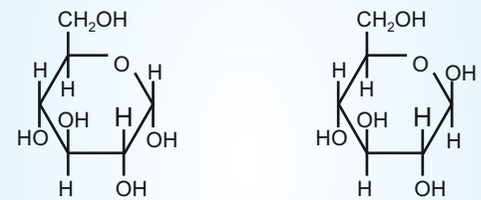


Cyclic Structure of Glucose

- The given observations could not explain chain structure of glucose
  - (i) It does not react with $NaHSO_3$ or Schiff's reagent
  - (ii) Pentaacetate of glucose does not react with NH_2OH.
  - (iii) Glucose exist in two different crystalline forms, α and β forms.

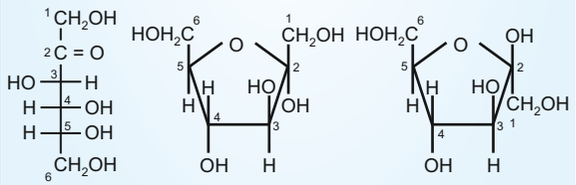


- α and β forms of glucose are called anomers. Six membered cyclic structure of glucose is called pyranose structure



(b) Fructose

- Fructose is a ketohexose
- Following structures have been assigned to this molecule



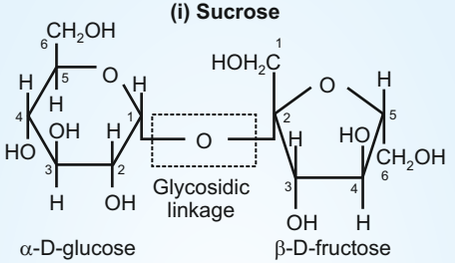
Tests of Glucose and Fructose

Both glucose and fructose reduce Tollen's reagent and Fehling's solution. They are also called reducing sugars.

2 DISACCHARIDES

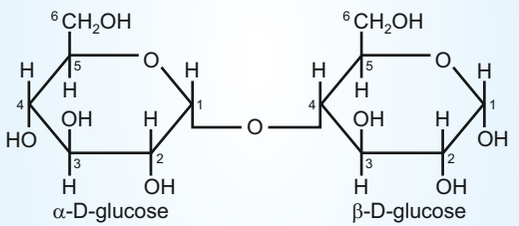
- Two monosaccharides are joined together by an oxide linkage formed by loss of water molecule forming a disaccharide. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

(i) Sucrose



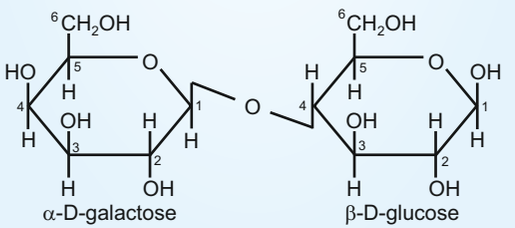
- It is dextrorotatory
- It is non reducing sugar

(ii) Maltose



- It is dextrorotatory
- It is reducing sugar
- It gives positive test with Tollen's reagent and Fehling's solution

(iii) Lactose



- It is dextrorotatory and is a reducing sugar
- It reduces Tollen's reagent and Fehling's solution

3 POLYSACCHARIDES

(i) Starch → Amylose (15-20% of starch)
→ Amylopectin (80-85% of starch)

- Amylose is water soluble component. It is long unbranched chain with 200-1000 α-D-(+) glucose units.
- Amylopectin is water insoluble component. It is branched chain polymer of α-D-glucose units.

(ii) Cellulose

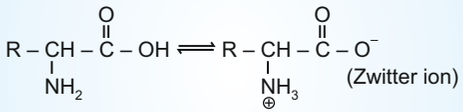
- It is a straight chain polysaccharide
- It is composed of β-D-glucose units

(iii) Glycogen

- It is called animal starch.
- Its structure is similar to amylopectin and is rather more highly branched.

4 PROTEINS

- All proteins are polymers of α-amino acid
- The amino acids which can be synthesised in the body, are known as non-essential amino acids.
- The amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids.
- In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as zwitter ion



Structure of Proteins

- Proteins can be classified into two types on the basis of their molecular shape

(a) Fibrous proteins:

- The polypeptide chains run parallel and held together by hydrogen and disulphides bonds giving fibre like structure
- They are insoluble in water e.g. keratin, myosin

(b) Globular proteins:

- In this case polypeptide chains coil around to give a spherical shape
- They are soluble in water e.g. insulin, globulin

5 VITAMINS

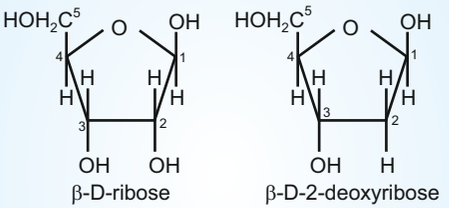
(i) Fat soluble vitamins: vitamins are soluble in fat. These are vitamins A, D, E and K.

(ii) Water soluble vitamins: B group vitamins and vitamin C are water soluble vitamins.

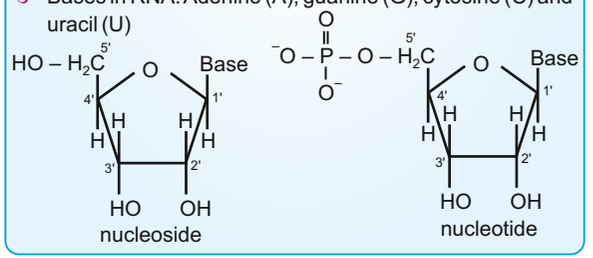
	Name of Vitamin	Deficiency Diseases
1.	Vitamin A	Xerophthalmia
2.	Vitamin B_1 (Thiamine)	Beri beri
3.	Vitamin B_2 (Riboflavin)	Cheilosis
4.	Vitamin B_{12}	Pernicious anaemia
5.	Vitamin C (Ascorbic acid)	Scurvy
6.	Vitamin D	Rickets (in children) osteomalacia (in adults)
7.	Vitamin K	Increased blood clotting time

6 NUCLEIC ACIDS

- Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compound (called bases)
- In DNA molecule, the sugar moiety is β-D-2-deoxyribose whereas in RNA molecules, it is β-D-ribose



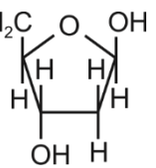
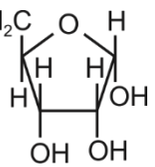
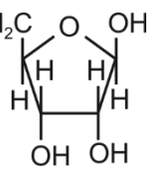
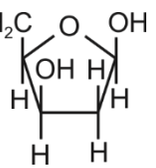
- Bases in DNA: Adenine (A), guanine (G), Cytosine (C) and thymine (T)
- Bases in RNA: Adenine (A), guanine (G), cytosine (C) and uracil (U)



Sharpen Your Understanding

1. Glucose does not react with [NCERT Pg. 415]
   (1) NH_2OH (2) Br_2 water
   (3) HCN (4) $NaHSO_3$
2. The compound which will not react with Tollen's reagent is [NCERT Pg. 417]
   (1) Sucrose (2) Glucose
   (3) Fructose (4) Maltose
3. Number of ^-OH group present in a sucrose molecule is [NCERT Pg. 417]
   (1) 9 (2) 10
   (3) 8 (4) 11
4. α-D-(+)-glucose and β-D-(+) glucose molecules are [NCERT Pg. 417]
   (1) Enantiomers (2) Anomers
   (3) Epimers (4) Homomers
5. Consider the following statements [NCERT Pg. 418]
   (a) Amylose and Amylopectin are components of starch
   (b) Amylopectin is insoluble in water
   (c) Amylose is long unbranched chain of α-D-(+)-glucose units
   The correct statements are
   (1) (a) & (b) only
   (2) (b) & (c) only
   (3) (a) & (c) only
   (4) (a), (b) & (c)
6. Incorrect statement among the following is [NCERT Pg. 419]
   (1) Cellulose is most abundant organic substance in plant kingdom
   (2) Cellulose is straight chain polysaccharide formed by β-D-glucose units
   (3) Glycogen is known as animal starch
   (4) Structure of Glycogen is similar to cellulose
7. Number of achiral carbons present in α-D- (–) fructofuranose structure is [NCERT Pg. 416]
   (1) 5 (2) 3
   (3) 4 (4) 2
8. Cyclic amino acid among the following is [NCERT Pg. 421]
   (1) Lysine (2) Proline
   (3) Cysteine (4) Serine
9. Which among the following is/are fibrous protein? [NCERT Pg. 422]
   (1) Keratin (2) Insulin
   (3) Myosin (4) Both (1) and (3)
10. Deficiency of which vitamin causes pernicious anaemia? [NCERT Pg. 426]
    (1) Vitamin B_6
    (2) Vitamin B_{12}
    (3) Thiamine
    (4) Riboflavin

NCERT Based MCQs

11. Monosaccharide units present in Lactose are [NCERT Pg. 418]
    (1) β-D-Glucose and β-D-Glucose
    (2) α-D-Glucose and β-D-Fructose
    (3) α-D-Glucose and α-D-Glucose
    (4) β-D-Galactose and β-D-Glucose
12. Water soluble vitamin among the following is [NCERT Pg. 426]
    (1) Vitamin C (2) Vitamin D
    (3) Vitamin K (4) Vitamin A
13. Sugar unit present in RNA is [NCERT Pg. 427]
    (1) 
    (2) 
    (3) 
    (4) 

14. The base which is absent in RNA is [NCERT Pg. 428]
(1) Guanine
(2) Cytosine
(3) Uracil
(4) Thymine

15. In a DNA strand, adenine forms hydrogen bond with [NCERT Pg. 429]
(1) Cytosine
(2) Guanine
(3) Thymine
(4) Uracil

16. Incorrect statement among the following is [NCERT Pg. 430, 429, 428]
(1) DNA is the chemical basis of heredity
(2) Nucleotides are joined together by phosphodiester linkage between 5′ and 3′ carbon atoms of the pentose sugar
(3) A unit formed by the attachment of a base to 1′ position of sugar is known as nucleotide
(4) Five nitrogen atoms are present in an adenine molecule

17. Which hormone is responsible for preparing the uterus for implantation of fertilized egg? [NCERT Pg. 430]
(1) Testosterone (2) Estradiol
(3) Progesterone (4) Thyroxine

18. Consider the following statements [NCERT Pg. 417]
(a) Sucrose on hydrolysis give equimolar mixture of D-glucose and D-fructose
(b) Two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C-1.
(c) Fructose is laevorotatory
The correct statements are
(1) (a) & (c) only
(2) (b) & (c) only
(3) (a) & (b) only
(4) (a), (b) & (c)

19. Deficiency of which vitamin causes rickets in children? [NCERT Pg. 426]
(1) Vitamin A
(2) Vitamin D
(3) Vitamin B_2
(4) Vitamin E

20. Which amino acid contains amide functional group? [NCERT Pg. 421]
(1) Glutamine
(2) Tyrosine
(3) Histidine
(4) Methionine

Thinking in Context

1. Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called _____ [NCERT Pg. 412]
2. Glucose on prolonged heating with HI, forms _____ [NCERT Pg. 413]
3. Glucose is oxidised to _____ on reaction with nitric acid. [NCERT Pg. 414]
4. Pentaacetate of glucose does not react with hydroxylamine indicating the absence of free _____ group. [NCERT Pg. 415]
5. The six membered cyclic structure of glucose is called pyranose structure, in analogy with _____. [NCERT Pg. 416]
6. Hydrolysis of _____ brings about a change in sign of rotation, from dextro to laevo and the product is named as invert sugar. [NCERT Pg. 417]
7. A linkage between two monosaccharide units through oxygen atom is called _____ linkage. [NCERT Pg. 417]
8. In amylopectin, branching occurs by _____ glycosidic linkage [NCERT Pg. 418]
9. The amino acids, which cannot be synthesised in the body and must be obtained through diet, are known as _____. [NCERT Pg. 421]
10. In _____ form, amino acids show amphoteric behaviour. [NCERT Pg. 422]

11. Except _____, all other naturally occurring α-amino acids are optically active [NCERT Pg. 420]
12. Deficiency of _____ causes Beri beri. [NCERT Pg. 426]
13. _____ are joined together by phosphodiester linkage between 5' and 3' carbon atoms of pentose sugar. [NCERT Pg. 428]
14. In DNA cytosine forms hydrogen bonds with _____. [NCERT Pg. 429]
15. In maltose _____ of one glucose (I) is linked to _____ of another glucose unit (II) [NCERT Pg. 417]
16. Glucose is oxidise to _____ by Br_2 water. [NCERT Pg. 413]
17. _____ is released in response to the rapid rise in blood glucose level [NCERT Pg. 430]
18. _____ are molecules that act as inter cellular messengers. [NCERT Pg. 430]
19. Low level of _____ in the diet may lead to hypothyroidism. [NCERT Pg. 430]
20. _____ Control the level of excretion of water and salt by the kidney. [NCERT Pg. 431]

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