

Maharashtra State Board
Class XII Chemistry
Board Paper – 2015 Solution

SECTION - I

1.

(i) **(c)** Boron

Boron (electronic configuration $1s^2 2s^2 2p^1$) is one electron deficient as compared to the valence electrons in the silicon atom. On adding boron to silicon, some atoms of boron occupy some sites of silicon atoms.

(ii) **(c)** $\Delta S_{\text{total}} = 0$

ΔS_{total} must be zero for the process at equilibrium.

(iii) **(a)** Number of solute particles

Colligative properties of solutions depend only on the number of solute particles.

(iv) **(d)** 4196

Moles of Na = $1.00/23.0 = 0.0435$

Cathode-half reaction will be



It states that for every one Faraday consumed, one mole of Na is liberated.

This means to get 0.0435 moles, we need to use 0.0435 Faraday.

We know that

1 Faraday = 96500 coulomb

0.0435 Faraday = 4197.75 coulomb

So, the nearest option is 4196.

(v) **(b)** $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$

The chemical composition of malachite is $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$.

(vi) **(c)** Bi

With the exception of Bismuth, all other elements exhibit allotropy.

(vii) **(a)** $k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$

The integrated rate equation for the first order reaction, $A \rightarrow \text{products}$

$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$

2.

(i)

(a) Enthalpy of fusion

The enthalpy change which accompanies the fusion of one mole of a solid without change in temperature at constant pressure is called its enthalpy of fusion.

(b) Enthalpy of atomisation

The enthalpy change accompanying the dissociation of all the molecules in one mole of gas phase into gaseous atoms is called enthalpy of atomisation.

(ii) Let 'V' be the volume of a dilute solution at an absolute temperature T containing 'W' grams of a substance with molecular mass 'M'.

Number of moles of the substance, $n = W/M$

Concentration of the solution, $C = n/V$

At constant temperature, by van't Hoff's law

$$\Pi \propto C$$

At constant concentration of the solution, by van't Hoff-Charles law

$$\Pi \propto T$$

Therefore, $\Pi \propto CT$

$$\Pi = CRT$$

Where R = gas constant

This is called the van't Hoff general solution equation.

Since $C = n/V$

$$\Pi = n R T/V$$

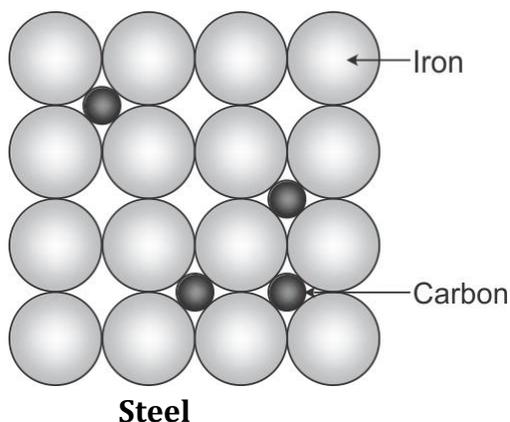
Therefore, $\Pi V = n R T$

Since $n = W/M$

Therefore, $\Pi V = WR T/M$

(iii) Pure iron is soft and malleable, whereas stainless steel is hard, strong, less ductile, shiny and bright in appearance.

Stainless steel is an interstitial alloy formed by introducing carbon atoms as impurity.



(iv) The integrated rate law for the first order reaction is given by the equation

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

Where $[A]_0$ = initial concentration of the reactant at $t = 0$

The concentration falls to $[A]_t$ at time t from the start of the reaction.

The concentration of the reactant falls to $[A]_0/2$ at time $t_{1/2}$.

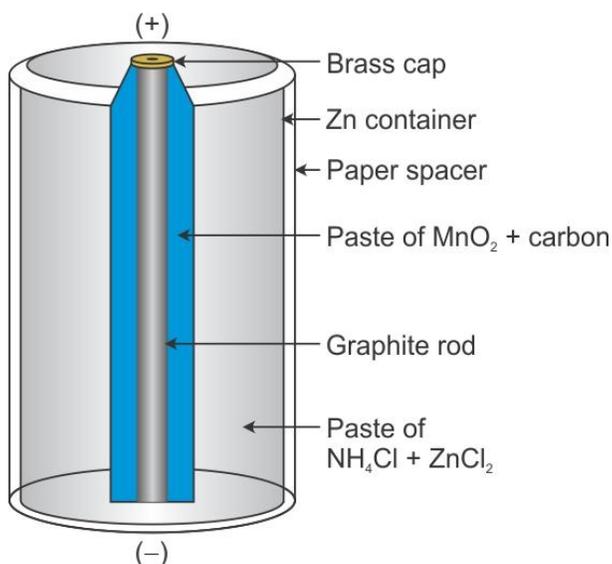
Therefore, $t = t_{1/2}$

$$[A]_t = [A]_0/2$$

So, the equation can be written as

$$\begin{aligned} k &= \frac{2.303}{t_{1/2}} \log_{10} \frac{[A]_0}{[A]_0/2} \\ &= \frac{2.303}{t_{1/2}} \log_{10} 2 \\ &= \frac{2.303}{t_{1/2}} \times 0.301 = \frac{0.693}{t_{1/2}} \\ t_{1/2} &= \frac{0.693}{k} \end{aligned}$$

(v)



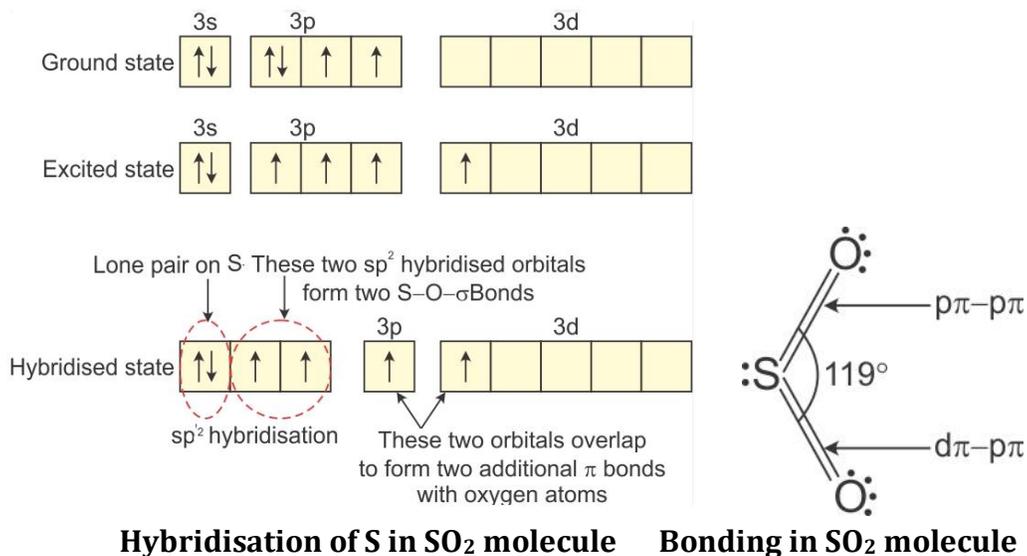
(vi) SO_2 molecule has a bent structure with an O-S-O bond angle of 119° .

Sulphur is sp^2 hybridised and the lone pair of electrons of sulphur reduces the bond angle from 120° to 119° .

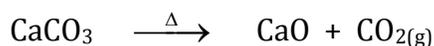
In the structure, each oxygen atom is attached to sulphur by an σ and a Π bond.

The σ bonds between S and O are formed by sp^2 -p overlap, while one of the Π bonds is formed from p Π - p Π overlap and other from p Π -d Π overlap.

Both S-O bonds are identical because of resonance.



(vii) Calcination is a process in which the ore is heated to a high temperature below its melting point in the absence of air or in a limited supply of air.



(viii) $\text{Cl} < \text{Cu} < \text{Ni} < \text{Al}$

Reason: Substances which have lower electrode potential are stronger reducing agents, while those which have high electrode potential are stronger oxidising agents.

3.

(i)

(a) $\Delta H = -110 \text{ kJ}$, $\Delta S = +40 \text{ JK}^{-1}$ at 400 K

$\Delta H = -ve$; heat is evolved in an exothermic reaction

In the above case, $\Delta H < 0$ and $\Delta S > 0$. Under these conditions, both ΔH and $T\Delta S$ terms will be negative, so ΔG will be negative regardless of the temperature.

So, the reaction will be spontaneous and exothermic.

(b) $\Delta H = +40 \text{ kJ}$, $\Delta S = -120 \text{ JK}^{-1}$ at 250 K

$\Delta H = +ve$; heat is absorbed in an endothermic reaction

In the above case, $\Delta H > 0$ and $\Delta S < 0$. Under these conditions, ΔG is always positive and the reaction is always non-spontaneous.

So, the reaction will be non-spontaneous and endothermic.

- (ii) Mass of solute (A), i.e. urea = 1.0×10^{-3} kg
 Molar mass of solute (A) = 60
 Mass of solvent in which solute A is dissolved = 0.0985 kg
 Mass of solute (B) = 1.6×10^{-3} kg
 Molar mass of solute (B) = ?
 Mass of solvent in which solute B is dissolved = 0.086 kg

$$\frac{\Delta T_{f_A}}{\Delta T_{f_B}} = \frac{m_A}{m_B}$$

$$\frac{0.211}{0.34} = \frac{\frac{\text{Mass of solute(A)}}{\text{Molecular mass of solute(A)} \times \text{Kg of solvent}}}{\frac{\text{Mass of solute(B)}}{\text{Molecular mass of solute(B)} \times \text{Kg of solvent}}}$$

$$\frac{0.211}{0.34} = \frac{\frac{1 \times 10^{-3}}{60 \times 0.0985}}{\frac{1.6 \times 10^{-3}}{\text{Molecular mass of solute(B)} \times 0.086}}$$

$$\frac{0.211}{0.34} = \frac{1 \times 10^{-3} \times \text{Molecular mass of solute(B)} \times 0.086}{60 \times 0.0985 \times 1.6 \times 10^{-3}}$$

$$\text{Molecular mass of solute(B)} = \frac{0.211 \times 60 \times 0.0985 \times 1.6 \times 10^{-3}}{0.34 \times 1 \times 10^{-3} \times 0.086} = 68.24$$

Molar mass of another solute = 68.24

- (iii) $t_{1/2} = 3$ hours

Now we know that,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3} = 0.231 \text{ h}^{-1}$$

Put above value in the formula of first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{8} \log \frac{[R]_0}{[R]}$$

So,

$$\log \frac{[R]_0}{[R]} = \frac{0.231 \times 8}{2.303} = 0.8024$$

Taking antilog on both sides,

$$\frac{[R]_0}{[R]} = 6.3445$$

$$\frac{[R]}{[R]_0} = 0.158$$

Fraction of the sample of sucrose remaining after 8 hours = 0.158

- (iv) Nitrogen shows anomalous behaviour as follows:
- Nitrogen is a gas, whereas the other members of the family are solids.
 - Nitrogen is diatomic, while the other elements such as phosphorus and arsenic form tetra-atomic molecules (P_4 , As_4).
 - Nitrogen forms five types of oxides (N_2O , NO , N_2O_3 , N_2O_4 and N_2O_5), while the other members form two types of oxides—trioxides and pentoxides.
 - Hydrides of nitrogen consist of H-bonding, which is absent in members of other elements.
 - Nitrogen does not show penta-covalency because of the absence of d-orbitals, but all other elements show penta-covalency.
 - Nitrogen does not form complexes because of the absence of d-orbitals, while the other elements show complex formation (e.g. $[PCl_6]^-$, $[AsCl_6]^-$).
 - The hydride of nitrogen (NH_3) is highly basic in nature, whereas the hydrides of other elements are slightly basic.

4.

(i) Calculation of atomic radius of niobium:

Crystal structure of Niobium = bcc

Density (d) = 8.55 kg dm^{-3}

Atomic mass of Niobium = 93

$$d = \frac{n \times M}{V \times N_A}$$

No. of atoms per unit cell (n) in bcc = 2

Total volume of unit cell = a^3

$$d = \frac{2 \times 93}{a^3 \times 6.023 \times 10^{23}}$$

$$a^3 = \frac{2 \times 93}{8.55 \times 6.023 \times 10^{23}} = 36.12 \times 10^{-24}$$

$$a = \sqrt[3]{36.12 \times 10^{-24}}$$

$$a = 3.305 \times 10^{-8}$$

In BCC unit cell,

$$r = \frac{\sqrt{3} \times a}{4} = \frac{\sqrt{3} \times 3.305 \times 10^{-8}}{4} = 1.431 \times 10^{-8} \text{ cm or } 143.1 \text{ pm}$$

First law of thermodynamics:

If the quantity of heat supplied to a system is capable of doing work, then the quantity of heat absorbed by the system is equal to the sum of the increase in the internal energy of the system and the external work done by it.

The equation which supports the first law of thermodynamics mathematically is

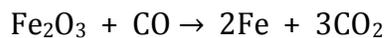
$$\Delta U = q + w$$

When expressed in the differential form, the same relationship takes the following form:

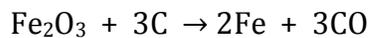
$$dQ = dU + dL$$

Zone of reduction:

Carbon monoxide reduces ferric oxide to spongy iron (porous solid) at about 900 K.



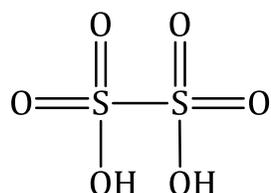
A small amount of ferric oxide is also reduced to iron by carbon.



(ii)

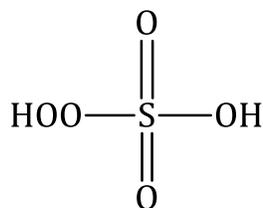
(1) Dithionic acid

Molecular formula: $\text{H}_2\text{S}_2\text{O}_6$



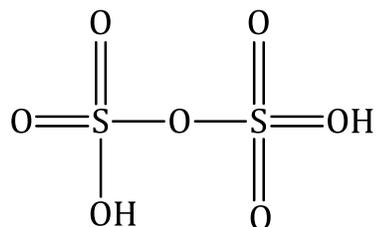
(2) Peroxymonosulphuric acid

Molecular formula: H_2SO_5



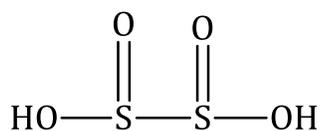
(3) Pyrosulphuric acid

Molecular formula: $\text{H}_2\text{S}_2\text{O}_7$



(4) Dithionous acid

Molecular formula: $\text{H}_2\text{S}_2\text{O}_4$



According to Nernst equation

$$E = E_{\text{cell}}^0 - \frac{0.059}{2} \log \frac{[\text{Mg}^{+2}]}{[\text{Sn}^{+2}]}$$

$$[\text{Mg}^{+2}] = 0.06 \text{ M} \quad [\text{Sn}^{+2}] = 0.04 \text{ M}$$

$$E = 2.23 - \frac{0.059}{2} \log \frac{0.06}{0.04}$$

$$\begin{aligned}
E &= 2.23 - \frac{0.059}{2} \log \left(\frac{3 \times 10^{-2}}{2 \times 10^{-2}} \right) \\
&= 2.23 - \frac{0.059}{2} \log 1.5 \\
&= 2.23 - \left(\frac{0.059}{2} \times (0.1760) \right) \\
&= 2.23 - 0.0052 \\
&= 2.225
\end{aligned}$$

$$E_{\text{cell}} = 2.225$$

Now $\Delta G = -nFE$

$$n = 2 \text{ mol}, F = 96500 \text{ C}, E = 2.225$$

$$\Delta G = -2 \times 96500 \times 2.225$$

$$= -429425 \text{ CV}$$

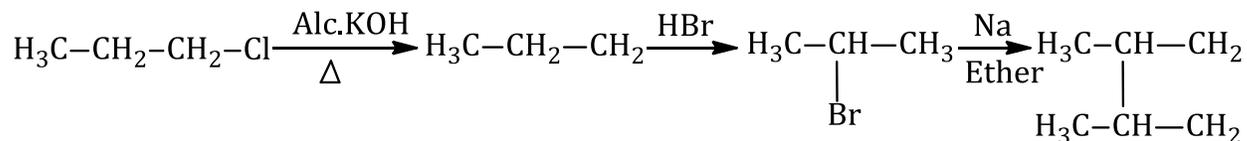
$$\Delta G = -429.425 \text{ kJ}$$

The reaction is spontaneous.

SECTION - II

5.

(i) **(b)** 2, 3-dimethyl butane



Propyl chloride

Propene

2-bromo propane

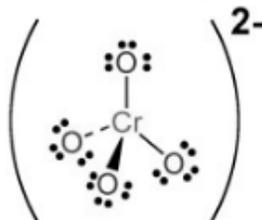
2,3 dimethyl butane

(ii) **(c)** $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{SO}_4$

$[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{SO}_4$ complex will give a white precipitate on treatment with a solution of barium nitrate. The white precipitate is of barium sulphate (BaSO_4).

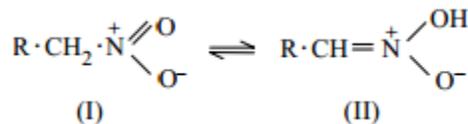
(iii) **(a)** Tetrahedral

The chromate anion CrO_4^{2-} has tetrahedral geometry.



(iv) **(b)** Tautomerism

Primary and secondary nitroalkanes containing α -hydrogen atoms show tautomerism. Here, the isomers are obtained by 1,3-migration of a proton from one polyvalent atom to the other within the same molecule.

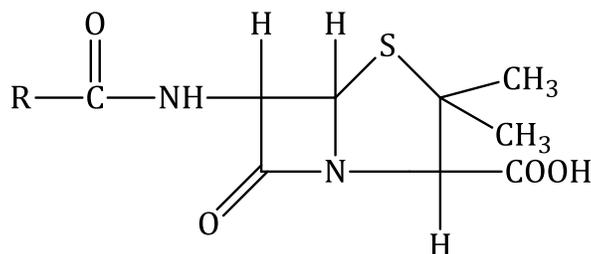


(v) **(c)** sp^2 hybridisation

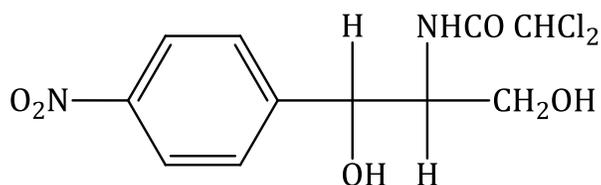
The carbon to which the hydroxyl group is bonded in phenol is sp^2 hybridised. The increased s-character of the carbon orbital used to form the C—O bond makes it more electron-withdrawing. Thus, conjugation with the aromatic ring would make the sp^2 hybridised oxygen atom more likely.

- (iii) An antibiotic is a drug derived from living matter or microorganisms which is used to kill or prevent the growth of other microorganisms. The antibiotics are classified into two types—bactericidal (killing bacteria) and bacteriostatic (inhibits growth of bacteria).

Examples of antibiotics:

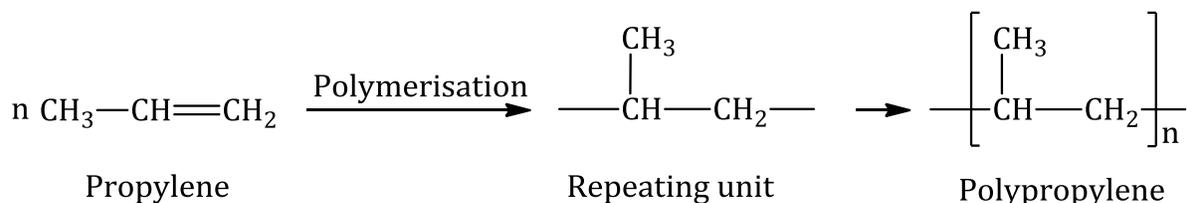


Penicillin (bactericidal)



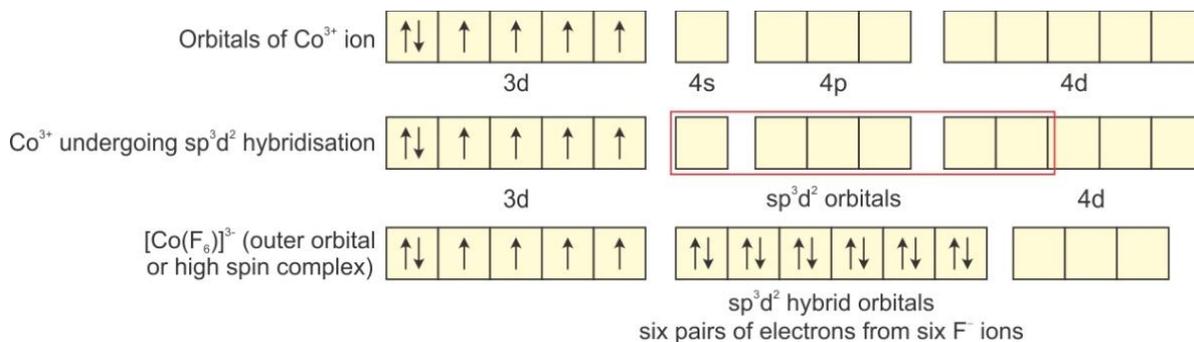
Chloramphenicol (bacteriostatic)

- (iv) The boiling points of carboxylic acids are higher than the corresponding alcohols because
- Carboxylic acids have a high boiling point because of their ability to form intermolecular hydrogen bonds.
 - Hydrogen bonds formed in carboxylic acids are stronger than those in alcohols.
 - The $-OH$ bond in $-COOH$ is more strongly polarised than the $-OH$ bond of alcohols. This is because of the presence of an electron-withdrawing carboxyl group in an adjacent position in carboxylic acids.
- (v) On the basis of molecular shape, proteins are classified into two types—fibrous proteins and globular proteins.
- Fibrous proteins:** They are insoluble in water, long, thread-like and tend to lie side by side to form fibres. The polypeptide chains are held together by hydrogen bonds. Examples: Collagen in tendons; keratin in hair, skin, nails, horn and feathers; myosin in muscle; fibroin in silk
 - Globular proteins:** They are soluble in water and aqueous solutions of bases, acids and salts. They are folded to form a spherical shape, have intramolecular hydrogen bonding and have weak intermolecular forces as compared to fibrous proteins.



7.

(i) The oxidation state of cobalt in this complex is +3. Hence, we have



F^- ion provides a weak ligand field and is unable to pair up the unpaired electrons of the 3d orbitals. Hence, six equivalent hybrid orbitals are obtained by mixing of one 4s, three 4p and two 4d orbitals. Six empty sp^3d^2 hybrid orbitals are filled up by six electron pairs provided by F^- ion. The highly paramagnetic nature of the complex further confirms the presence of four unpaired electrons.

As d-orbitals of the outermost shell take part in hybridisation, the complexes thus formed are called outer orbital complexes.

The IUPAC name of the complex $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$ is triamminetrinitro-N cobalt(III).

(ii) Lanthanoid contraction:

With an increasing atomic number in the lanthanoid series, there is a progressive decrease in the atomic as well as ionic radii of trivalent ions from La^{3+} to Lu^{3+} .

This regular decrease (contraction) in the size of the atoms and ions with increasing atomic number is known as lanthanoid contraction.

Effects of lanthanoid contraction:

(a) Effects on the basic strength of hydroxides: As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases. Thus, the basic strength decreases. Hence, $\text{La}(\text{OH})_3$ is most basic, while $\text{Lu}(\text{OH})_3$ is the least basic.

(b) Ionic radii of post lanthanoids: The elements which follow the lanthanoids in the third transition series are known as post lanthanoids. As a result of lanthanoid contraction, the atomic radii (size) of the elements which follow lanthanum (Hf, Ta, W etc.) are similar to those of the elements of the previous period. There is normal increase in size from Sc to Y to La. This trend disappears after the

lanthanoids, and pairs of elements Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc–Re (group 7) have almost identical sizes. These atoms possess similar number of valence electrons and similar properties. These pairs of elements are called ‘chemical twins’. The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series.

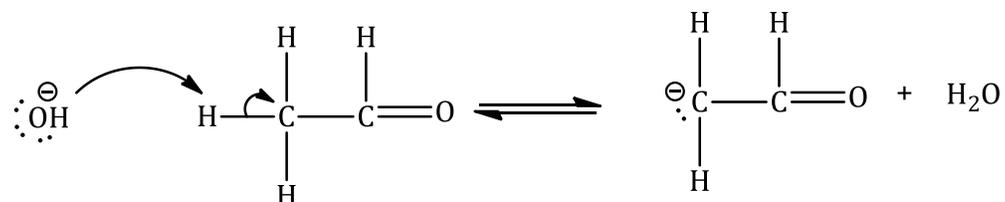
Group \ Series	4	5	6	7
1 st transition series	Ti (132 pm)	V (122 pm)	Cr (106 pm)	Mn (94 pm)
2 nd transition series	Zr (145 pm)	Nb (134 pm)	Mo (129 pm)	Tc (114 pm)
3 rd transition series	Hf (144 pm)	Ta (134 pm)	W (130 pm)	Re (114 pm)

(c) Difficulty in separation of lanthanoids: Because the changes in ionic radii (size of the ions) in the lanthanoids are very small, their chemical properties are similar. This makes the separation of the lanthanoids in the pure state difficult. However, lanthanoid contraction results in slight difference in the size of the lanthanoids which results in the differences in properties such as solubility, complex formation, hydration, basic character of their hydroxides etc. Because of these differences, the lanthanoids can be separated by the ion exchange method.

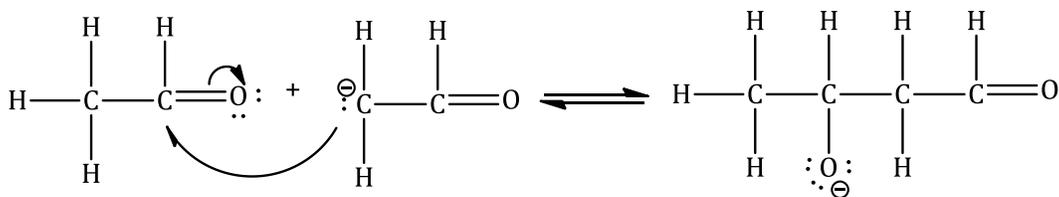
(iii) Aldol addition reaction:

'Aldol' is an abbreviation of aldehyde and alcohol. When the enolate of an aldehyde or a ketone reacts at the α -carbon with the carbonyl of another molecule under basic or acidic conditions to obtain β -hydroxy aldehyde or ketone, the reaction is called an aldol reaction.

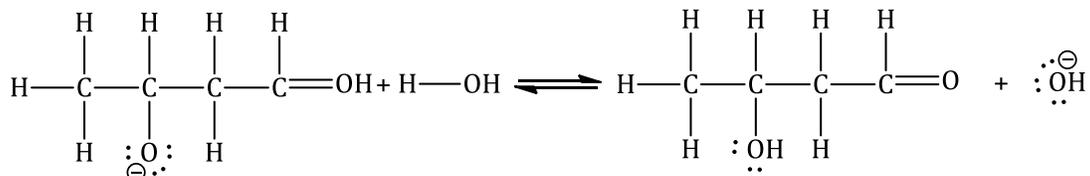
Step I: Base OH^- ion abstracts a hydrogen atom from an α -carbon of aldehyde to form carbanion.



Step II: The nucleophilic carbanion or enolate ion attacks the electrophilic carbonyl carbon of the second aldehyde molecule to form an intermediate alkoxide ion. A new C–C bond is formed.



Step III: Alkoxide ion abstracts a hydrogen ion from water to form β -hydroxy aldehyde. Base OH^- ion is regenerated.



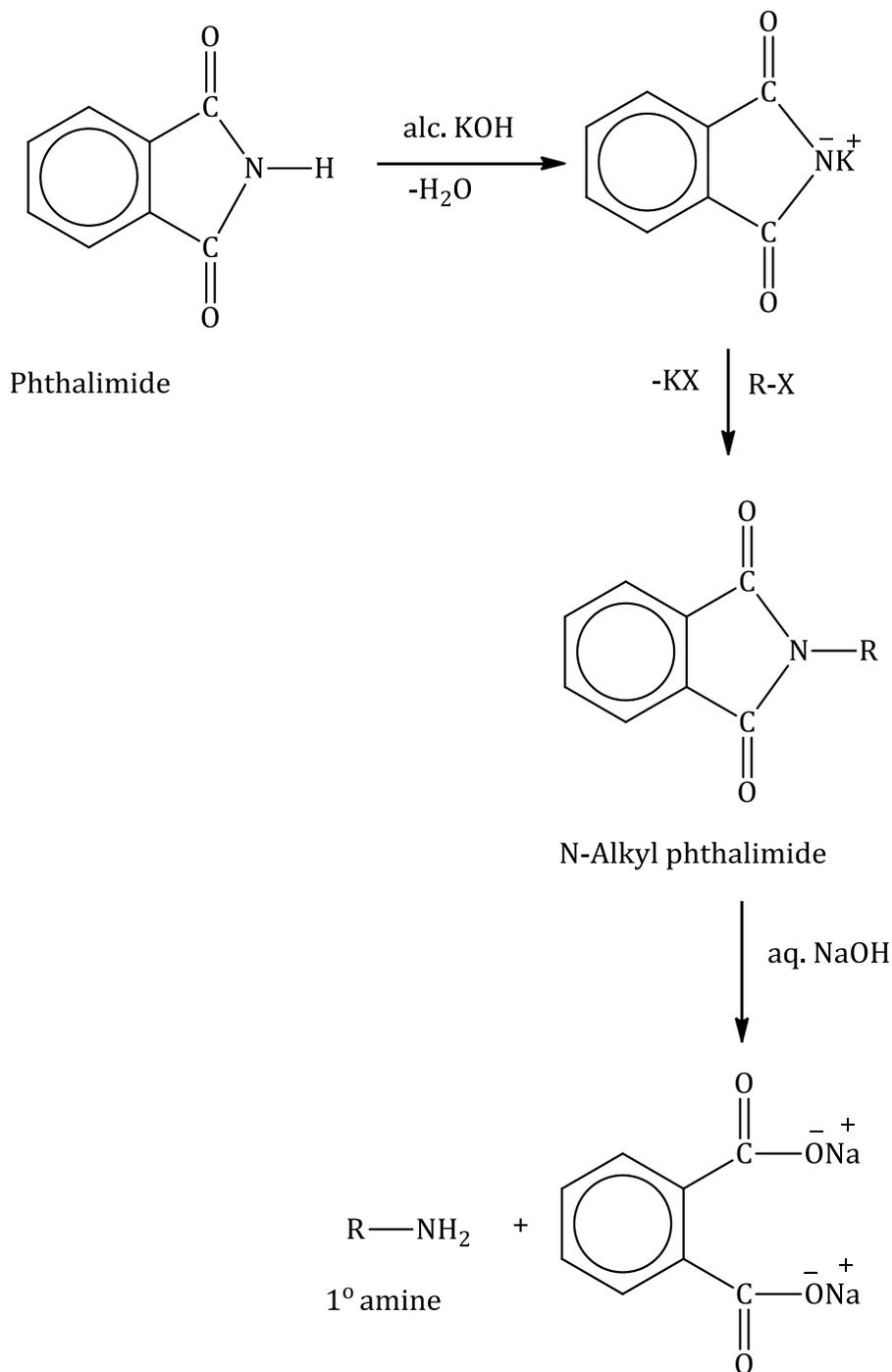
(iv) Carbohydrates are optically active polyhydroxy aldehydes or polyhydroxy ketones or the compounds which can be hydrolysed to polyhydroxy aldehydes or polyhydroxy ketones.

Carbohydrates are classified as

- (a) Reducing sugars: They reduce Fehling's solution and Tollens' reagent. All monosaccharides, whether aldoses or ketoses, are reducing sugars. Disaccharides in which aldehydic and ketonic groups are free behave as reducing sugars. Examples: Maltose, lactose
- (b) Non-reducing sugars: They do not reduce Fehling's solution and Tollens' reagent. Disaccharides in which aldehydic or ketonic groups are bonded behave as non-reducing sugars. Example: Sucrose

8.

- (i) Alkylation of phthalimide is known as Gabriel phthalimide synthesis. Phthalimide reacts with ethanolic potassium salt of phthalimide. In this step, N-H proton is removed to give imide ion. It is then heated with alkyl halide to give N-alkyl phthalimide, which gives a primary amine on alkaline hydrolysis.



Advantage: Overalkylation is avoided, so secondary or tertiary amines are not obtained.

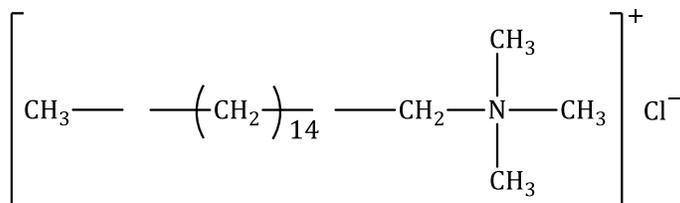
Limitation: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

Biodegradable polymers and non-biodegradable polymers: After a certain period of time, the natural polymers degrade on their own but synthetic polymers do not. These are non-biodegradable polymers and are resistant to environmental degradation processes and are accumulated as solid waste materials. Hence, efforts were made to synthesise biodegradable polymers to avoid environmental problems.

Example of biodegradable polymer: Dextron

Example of non-biodegradable polymer: 1-polyethylene

Cationic detergents: Cationic detergents are quaternary ammonium salts of amines with chlorides, acetates or bromides. They have cations at the soluble ends of the chain. Anions are chlorides, acetates or bromides, and cations are long chain hydrocarbons with a positive charge on the nitrogen atom. They are used as germicides and are expensive, for example, cetyltrimethyl ammonium chloride is used in hair conditioners. Hence, these cationic detergents are alkyl ammonium salts.

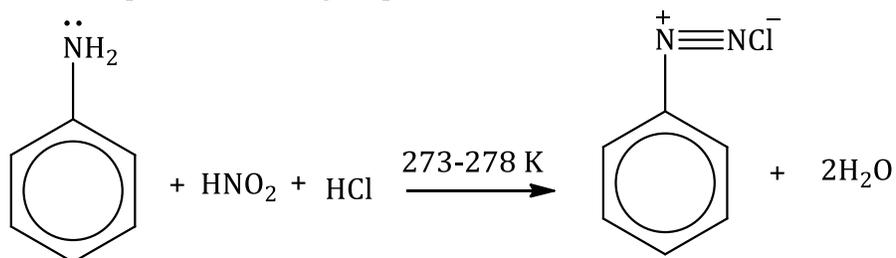


n-hexadecyl trimethyl
ammonium chloride or
(cetyltrimethyl ammonium chloride)

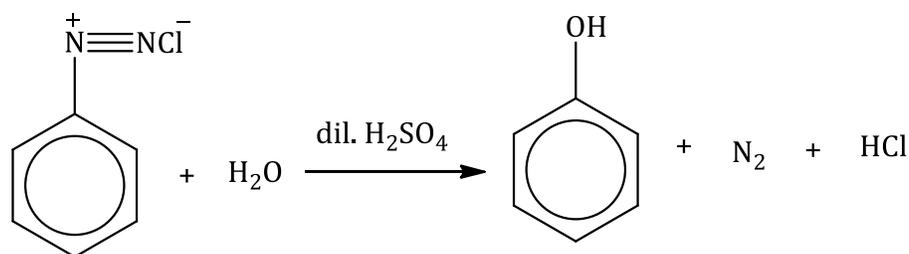
(ii) Preparation of carbolic acid from

(1) Aniline

When aniline (a primary aromatic amine) is treated with nitrous acid (NaNO_2 and HCl) under ice cold conditions, it gives benzene diazonium salt. This process is called diazotization. The aqueous solution of diazonium salt is hydrolysed with dilute sulphuric acid to give phenol. The reaction can be shown as follows:



Benzene diazonium chloride

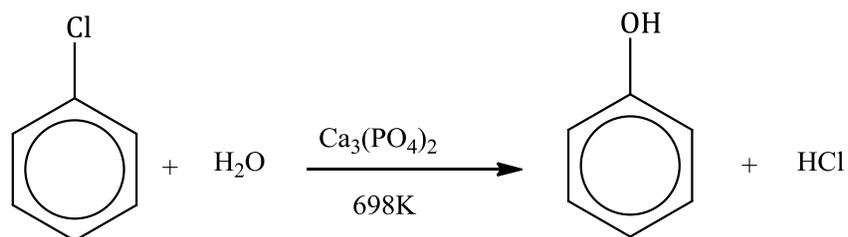


Benzene diazonium chloride

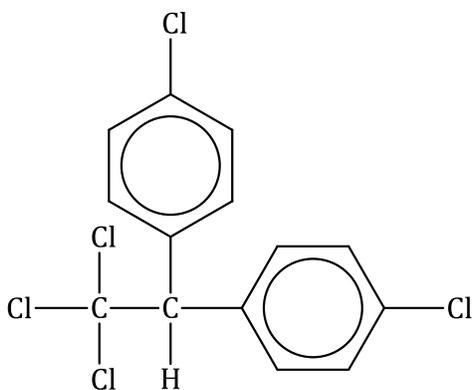
Phenol

(2) Chlorobenzene and steam at 698 K

Phenol is obtained by heating chlorobenzene with steam at 698 K using $\text{Ca}_3(\text{PO}_4)_2$ or SiO_2 as a catalyst. The hydrolysis can also be affected by water in the presence of copper as a catalyst at 673 K and under pressure.



Structure of dichlorodiphenyltrichloroethane (DDT) is as follows:



Physical properties of carbolic acid:

- (a) Pure phenol is a colourless, crystalline solid.
- (b) Phenol has characteristic smell known as phenolic or carbolic odour.
- (c) Melting point of phenol is 315 K.
- (d) Boiling point of phenol is 455 K.