



Rao IIT Academy

Symbol of Excellence and Perfection

HSC - BOARD - 2015

Date: 04.03.2015

CHEMISTRY (55) - SOLUTIONS

SECTION - I

Q.1

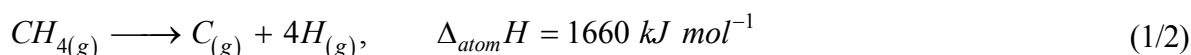
- (i) (b) Boron
 (ii) (c) $\Delta S_{total} = 0$
 (iii) (a) Number of solute particles
 (iv) (d) 4196
 (v) (b) $Cu(OH)_2 \cdot CuCO_3$
 (vi) (c) Bi
 (vii) (b) $K = -\frac{1}{t} \ln \frac{[A]_t}{[A]_0}$

Q.2

- (i) (a) **Enthalpy of fusion** : The enthalpy change that accompanies the fusion of one mole of a solid into liquid without change in temperature at constant pressure is called enthalpy of fusion. It is denoted by the symbol $\Delta_{fus}H$. (1/2)



- (b) **Enthalpy of atomization** : The enthalpy change accompanying the dissociation of all the molecules in one mole of gas-phase substance into gaseous atoms is called enthalpy of atomization. It is denoted as $\Delta_{atom}H$. (1/2)



- (ii) From van't Hoff-Boyle's law:

$$\pi \propto \frac{1}{V} \quad \dots(i) \quad (1/2)$$

From van't Hoff-charle's law:

$$\pi \propto T \quad \dots(ii) \quad (1/2)$$

Combining (i) & (ii) we get

$$\pi \propto \frac{T}{V} \quad \text{or} \quad \pi V = RT \quad (1/2)$$

Where R is gas constant ($R = 8.31 \text{ JK}^{-1} \text{ mol}^{-1}$)

If V is the volume of solution containing n moles of solute then

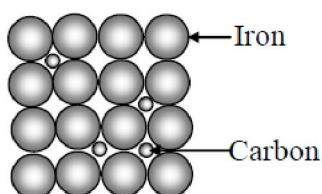
$$\pi V = nRT \quad \text{or} \quad \pi = \frac{n}{V} RT \quad \pi = CRT \quad (1/2)$$

Where, concentration $C = \frac{n}{V}$ is the number of solute per litre of solution.

(iii) **Impurity defect:**

- The impurity defect occurs when a regular cation of the crystal is replaced by some different cation.
- If the impurity cation is substituted in place of regular cation, it is called substitution impurity defect.
- If the impurity is present in the interstitial positions, it is called interstitial impurity defect.
- Stainless steel is an interstitial alloy formed by introducing carbon atom as impurity.
- The original properties of crystalline solid are almost completely changed due to impurity defect. (1)

Eg. Pure iron is soft malleable and ductile while stainless steel is hard, stronger, less ductile, shiny and bright in appearance.



Stainless steel

(1)

 (iv) **Half life of a reaction** is defined as the time needed for the reactant concentration to fall to one half of its initial value.

For the first order reaction $A \longrightarrow \text{products}$, the integrated rate law is given as follows :

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t} \dots\dots\dots(1) \quad (1/2)$$

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

$[A]_t$ = concentration of the reactant at time t

$$\text{At } t = t_{1/2} \quad [A]_t = \frac{[A]_0}{2} \quad (1/2)$$

Equation (1) becomes,

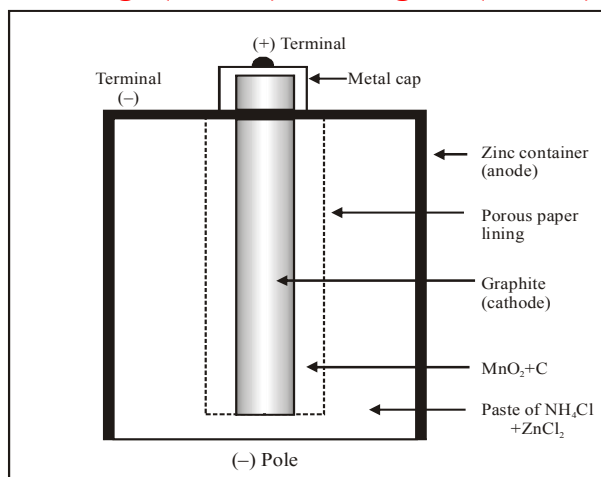
$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{[A]_0}{[A]_0 / 2}$$

$$\therefore t_{1/2} = \frac{2.303}{k} \log_{10} 2 = \frac{2.303}{k} \times 0.301 = \frac{0.693}{k} \quad (1/2)$$

$$\therefore t_{1/2} = \frac{0.693}{k} \quad (1/2)$$

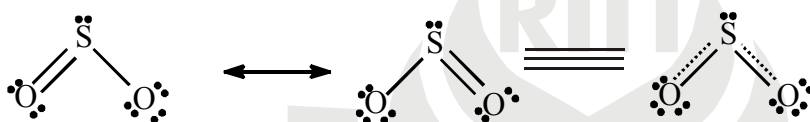
The half life of a first order equation is calculated from the rate constant and vice versa.

(v) Labelling - (1 Mark) Diagram (1 Mark)



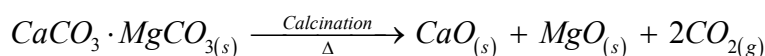
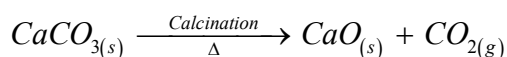
Dry cell

- (vi) Sulphur in SO_2 involves sp^2 hybridisation. Two of these sp^2 orbitals form two σ bonds with oxygen atom by overlap of sp^2 of S atom with $2p$ of two O atoms. The remaining two unhybridised orbitals of S form $p\pi - p\pi$ and $p\pi - d\pi$ double bonds with two O atoms. So, SO_2 has the two S–O bonds as shown in figure. (1)



The SO_2 molecule is angular O–S–O bond angle is 119° . It is reduced from 120° to 119° due to presence of one lone pair of electrons.

- (vii) **Calcination** : This is a process in which the ore of metal is heated to a high temperature below the melting point of metal in absence of air or limited supply of air. During calcination the organic matter, moisture, volatile impurities like carbon dioxide and sulphur dioxide are expelled from the ore which makes the ore porous. (1)



- (viii) Increasing strength is $\text{Cl} < \text{Cu} < \text{Ni} < \text{Al}$ (1)

Reducing strength $\propto \frac{1}{E^0 \text{ values}}$ because negative potential indicates most reducing element. (1)

Q.3

(i) **Given:**

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

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

To find: Whether the reactions are exothermic or endothermic and spontaneous or non-spontaneous.

Formula : $\Delta G = \Delta H - T\Delta S$ (1)

Calculation : (a) $\Delta S = +40 \text{ J/K} = 0.04 \text{ kJ/K}$ (1/2)

$$\Delta H = -110 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -110 - (400 \times 0.04)$$

$$= -110 - 16$$

$$= -126 \text{ kJ}$$

Because ΔG is negative, the reaction is **spontaneous** and the negative value of ΔH indicates that the reaction is **exothermic**. (1/2)

(b) $\Delta S = -120 \text{ J/K} = -0.120 \text{ kJ/K}$ (1/2)

$$\Delta H = +40 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = +40 - (250 \times -0.120)$$

$$= 40 + 30$$

$$= 70 \text{ kJ}$$

As ΔG is positive, the reaction is **non-spontaneous** and the positive value of ΔH indicates that the reaction is **endothermic**. (1/2)(ii) First calculate molality of urea solution, then calculate K_f for unknown solvent and molar mass of unknown compound.

Molar mass of urea = $14 + 2 + 12 + 16 + 14 + 2 = 60 \text{ g mol}^{-1} = 60 \times 10^{-3} \text{ kg mol}^{-1}$ (1/2)

(a) Molality of urea solution,

$$m = \frac{\text{mass of urea in kg}}{\text{molar mass urea} \times \text{mass of solvent in kg}}$$
 (1/2)

$$= \frac{1.0 \times 10^{-3} \text{ kg}}{60 \times 10^{-3} \text{ kg mol}^{-1} \times 98.5 \times 10^{-3} \text{ kg}}$$

$$= 0.1692 \text{ mol kg}^{-1}$$

(b) $K_f = \frac{\Delta T_f}{m} = \frac{0.211 \text{ K}}{0.1692 \text{ mol kg}^{-1}} = 1.247 \text{ K kg mol}^{-1}$ (1/2)

(c) $M_2 = \frac{K_f \times W_2}{\Delta T_f \times W_1}$ (1/2)

$$= \frac{1.247 \text{ K kg mol}^{-1} \times 1.60 \times 10^{-3} \text{ kg}}{0.34 \text{ K} \times 86.0 \times 10^{-3} \text{ kg}}$$

$$= 68.23 \times 10^{-3} \text{ kg mol}^{-1} \quad (1/2)$$

$$= 68.23 \text{ g mol}^{-1} \quad (1/2)$$

$$(iii) \quad t_{1/2} = 3 \text{ hrs} \quad t = 8 \text{ hrs} \quad \frac{[A]_t}{[A]_0} = ?$$

$$\therefore t = \frac{2.303}{0.693} \times t_{1/2} \times \log_{10} \frac{[A]_0}{[A]_t} \quad (1)$$

$$\therefore 8 = \frac{2.303}{0.693} \times 3 \times \log_{10} \frac{[A]_0}{[A]_t}$$

$$\therefore \log \frac{[A]_0}{[A]_t} = \frac{8 \times 0.693}{2.303 \times 3}$$

$$\log \frac{[A]_0}{[A]_t} = 0.8024 \quad (1)$$

$$\frac{[A]_0}{[A]_t} = 6.3445 \quad (1/2)$$

$$\therefore \frac{[A]_t}{[A]_0} = 0.1576 \quad (1/2)$$

(iv) **Anomalous properties of Nitrogen: (ANY SIX POINTS 3 MARKS)**

- Nitrogen is a gas at room temperature while the rest of the members of the family are solids.
- Nitrogen exists as diatomic molecule (N_2), whereas the other elements exist as tetratomic molecules (As_4, Sb_4, P_4 etc).
- Nitrogen can form hydrogen bonds in its hydride compounds due to small size and high electronegativity and rest of the members do not form hydrogen bonds due to small electronegativities and larger size.
- Nitrogen forms $p\pi - p\pi$ multiple bonds. Other elements of the group form multiple bonds through $d\pi - p\pi$ overlapping.
- Nitrogen shows all oxidation states from -3 to $+5$. The other group 15 elements show limited number of oxidation states.
- The trihalides of nitrogen (except NF_3) are unstable. Trihalides of other group 15 elements are stable.
- The hydride of nitrogen (NH_3) is more stable and more basic than the hydrides of the other members of the family.
- Nitrogen does not exhibit pentavalency in its compounds while other members show pentavalency.
- Nitrogen does not form coordination compounds due to absence of d-orbitals. Other group 15 elements form coordination compounds.

Q.4

(i) (a) **Given :**

Atomic mass (M) = 93 a.m.u.

Density (d) = 8.55 kg dm⁻³**To find:** Atomic radius (r) = ?

$$\text{Formula : } d = \frac{zM}{a^3 \cdot N_A}$$

$$\text{i.e. } a^3 = \frac{z \cdot M}{d \cdot N_A} \quad (1)$$

Calculation : Since it is a bcc arrangement, the number of atoms per unit cell (z) = 2

$$a^3 = \frac{2 \times 93 \text{ g mol}^{-1}}{8.55 \times 6.023 \times 10^{23} \text{ mol}^{-1}} \quad (1/2)$$

$$a^3 = \frac{186 \text{ g}}{51.50 \times 10^{23}}$$

$$= 3.61 \times 10^{-23} = 36.1 \times 10^{-24} \text{ cm}^3$$

$$\begin{aligned} \therefore a &= (36.1 \times 10^{-24})^{1/3} \\ &= 3.304 \times 10^{-8} \text{ cm} \\ &= 330.4 \times 10^{-10} \text{ cm} = 330.4 \text{ pm} \end{aligned} \quad (1/2)$$

$$\text{For body-centred cubic, } r = \frac{\sqrt{3}}{4} a = 0.433 a \quad (1/2)$$

$$= 0.433 \times 330.4 = 14.3 \text{ nm} \quad (1/2)$$

Atomic radius of niobium is 14.3 nm

(b) Energy can neither be created nor be destroyed although it can be transformed from one form to another. Whenever energy in one form disappears an equal amount of energy some other form reappears. (1)

$$\boxed{\Delta U = q + W} \quad (1)$$

This is mathematical expression for first law of thermodynamics.

(c) **Zone reduction:** At about 900°C, CO reduces*Fe*₂*O*₃ to spongy (or porous) iron.Carbon also reduces partially *Fe*₂*O*₃ to Fe

(ii) (a) (1) Dithionic acid ($H_2S_2O_6$)

 (2) Peroxy monosulphuric acid (H_2SO_5)

 (3) Pyrosulphuric acid ($H_2S_2O_7$)

 (4) Dithionous acid ($H_2S_2O_4$)

 (b) $Mg_{(s)} + Sn_{(aq)}^{2+} \rightarrow Mg_{(aq)}^{2+} + Sn_{(s)}$

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

$$Q = \frac{[Mg^{2+}]}{[Sn^{2+}]} = \frac{0.06}{0.04} = 1.5 \quad (1)$$

$$E_{cell}^0 = 2.23 \text{ V}$$

$$R = 8.314 \text{ Jk}^{-1} \text{ mol}^{-1}$$

$$T = 28^\circ\text{C} = 28 + 273 = 301 \text{ K}$$

$$n = 2$$

$$F = 96500 \text{ C/mol } e^-$$

$$\therefore E_{cell} = E_{cell}^0 - \frac{2.303 RT}{nF} \log_{10} Q \quad (1/2)$$

$$= 2.23 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \log_{10} (1.5)$$

$$= 2.23 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \times 0.1760$$

$$= 2.23 - 0.005255$$

$$\boxed{E_{cell} = 2.2247 \text{ V}} \quad (1/2)$$

$$\Delta G = -nFE_{cell} \quad (1/2)$$

$$= -2 \times 96500 \times 2.2247$$

$$\Delta G = -429367 J$$

$\therefore \Delta G$ is **negative** therefore reaction is **spontaneous**.

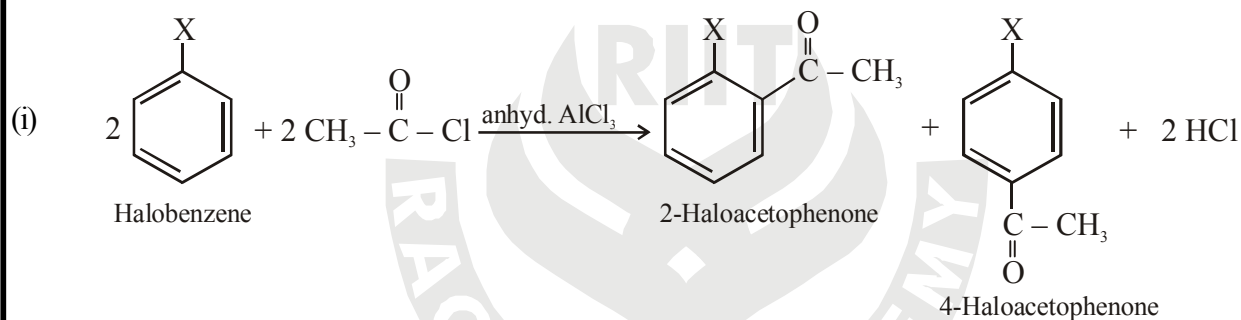
(1/2)

SECTION - II

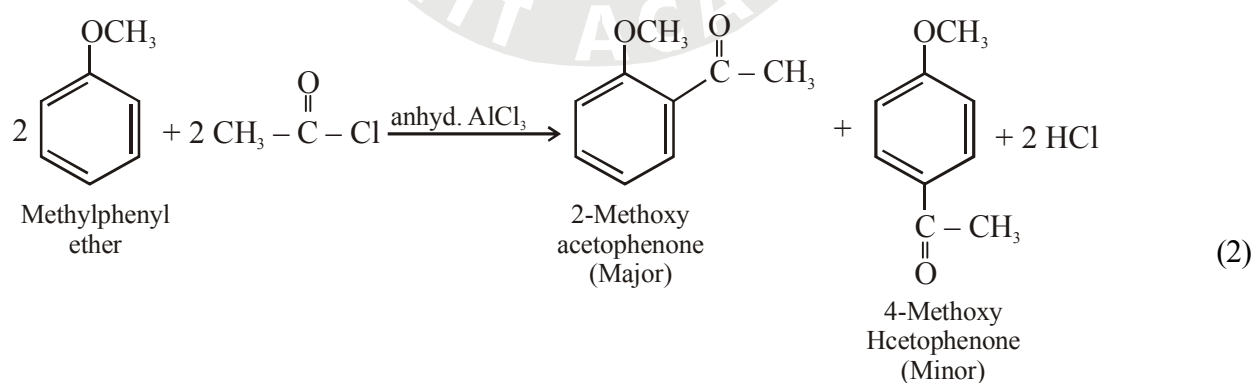
Q.5

- (i) (b) 2, 3 - dimethylbutane
 (ii) (c) $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{SO}_4$
 (iii) (a) Tetrahedral
 (iv) (b) tautomerism
 (v) (c) sp^2 -hybridisation
 (vi) (c) Trichloroacetic acid
 (vii) (d) B

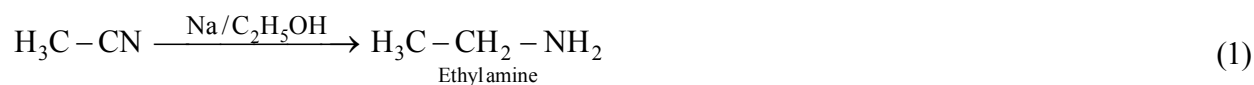
Q.6



OR



- (ii) Ethylamine from methyl iodide



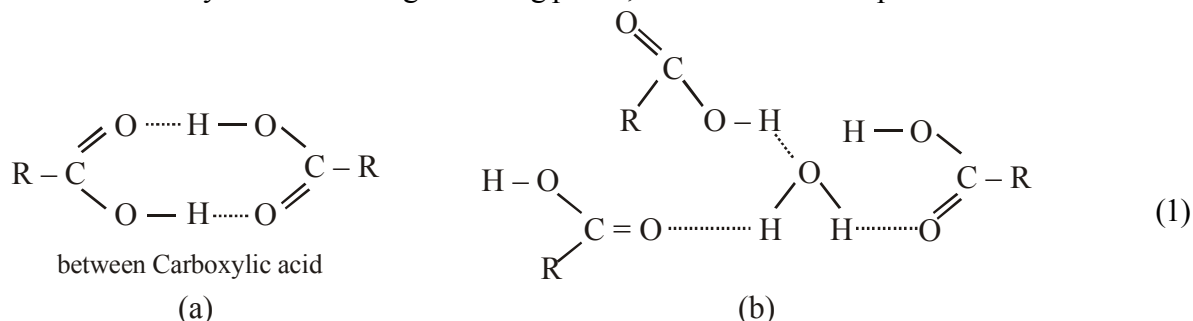
(iii) Antibiotics is a drug derived from living matter or micro-organism, used to kill or prevent the growth of other micro-organisms. (1)

eg. Penicillin, chloramphenicol, etc. (1)

(iv) (a) The carboxylic acid possess intermolecular hydrogen bonding as a result which they exist as dimer. (1)

(b) These hydrogen bonds are so strong that they are not broken completely even in vapour phase. (1)

(c) Thus the carboxylic acids have higher boiling points, than alcohol of comparable molecular masses. (1)



(v) **Proteins are classified on the basis of molecular shapes as follows:**

(a) **Fibrous proteins :** When the polypeptide chains lie parallel or side by side to form fibre-like structure, the protein is fibrous in shape. The molecules are held together at many points by hydrogen bonds or disulphide bonds. (1)

eg. Keratin in hair, nails and wool, fibroin in silk, myosin in muscle, collagen in tendons etc.

(b) **Globular proteins :** The polypeptide chains get folded to form globular structure. Intramolecular hydrogen bonding is present in globular proteins. The intermolecular forces are weaker than those present in fibrous proteins. (1)

eg. Insulin (from pancreas) thyroglobulin (from thyroid glands), haemoglobin, albumin, etc.

(vi) (a) Interstitial compounds are those which are formed when small atoms like H, C, N, B etc. are trapped inside the crystal lattice of metals. (1)

(b) They have melting point higher than metals due to stronger metal-non metal bonds or compared to metal-metal bonds in pure metals. (1)

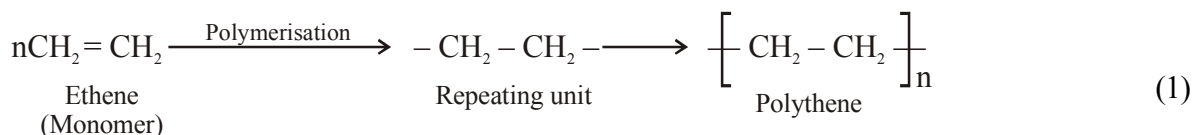
(vii) (a) Adipic Acid



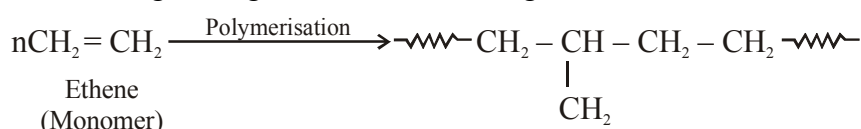
(b) α - Methyl butyraldehyde



(viii) (a) **Linear polymers :** They are made up of long continuous chains without any excess attachments (branches). The repeating units are joined together to form a long chain. Eg. Polythene, PVC



(b) Branched polymer : Monomer units not only combine to produce linear chain but also form branches of different length along with the main chain. eg. LDPE



Q.7

(i) (A) (a) Hexafluorocobaltate (III) ion, $[CoF_6]^{3-}$ is an anionic complex, the oxidation state of cobalt is +3 and the coordination number is 6.

(b) Electronic configuration : ${}_{27}Co[Ar]^{18} 3d^7 4s^2 4p^0 4d^0$ (1/2)

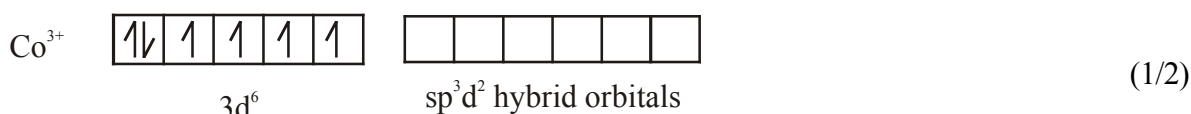
Electronic configuration : $Co^{3+}[Ar]^{18} 3d^6 4s^0 4p^0 4d^0$



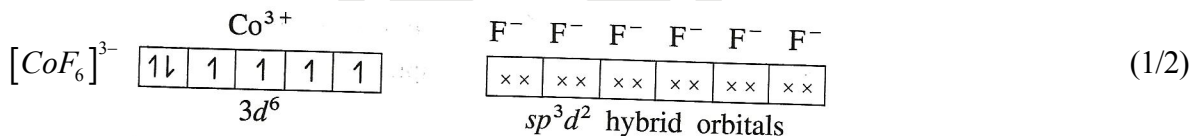
← sp^3d^2 hybridisation →

(c) Since F^- is a weak ligand, there is no spin pairing effect and Co^{3+} possesses 4 unpaired electrons.

(d) Since the coordination number is 6, the Co^{3+} ion gets six vacant orbitals by hybridisation of one 4s orbital, three 4p orbitals and two 4d orbitals forming six sp^3d^2 hybrid orbitals giving octahedral geometry.

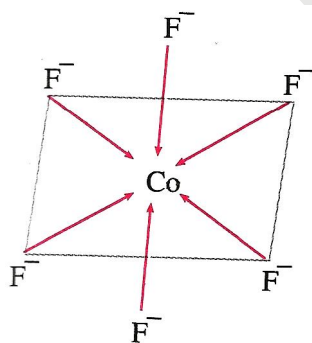


(e) 6 lone pairs of electrons from 6 F^- ligands are accommodated in the six vacant sp^3d^2 hybrid orbitals. Thus six hybrid orbitals of Co^{3+} overlap with filled orbitals of F^- forming 6 coordinate bonds giving octahedral geometry to the complex. It is an outer complex.



As the complex has 4 unpaired electron it is paramagnetic.

Magnetic moment μ is $\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.9 B.M$



(B) IUPAC name of $[Co(NO_2)_3(NH_3)_3]$ is Triamminetrinitrocobalt (III) (1)

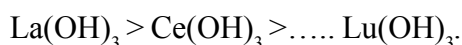
(ii) **Lanthanoid Contraction** : The atomic and Ionic Radii of lanthanoids shows gradual decrease with increase in atomic number. It is known as Lanthanoid Contraction. (1)

(A) **Decrease in Basicity**: (1)

(a) Because of lanthanoid contraction size of lanthanoid ions decreases regularly with increase in atomic number. As a result of decrease in size, the covalent character between lanthanoids ion and OH^- ions increases from La^{3+} to Lu^{3+} .

(b) The ionic character of M-OH bond decreases and covalent character of M-OH bond gradually increases. Therefore, the basic strength of the hydroxides decreases with increase in atomic number. Thus, $Lu(OH)_3$ is least basic while $La(OH)_3$ is most basic.

(c) Basicity and Ionic character of hydroxides decreases in the order of



(B) **Ionic radii of post lanthanoids :** (1/2)

The elements which follow the lanthanoids in the third transition series are known as postlanthanoids. There is a regular increase in size from Sc to Y to La. Similarly there will be increase in size in other groups as:



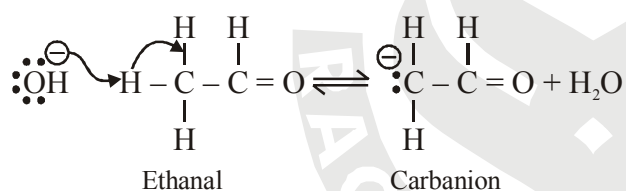
But after the lanthanoids the increase in radii from second to third transition series almost vanishes. Pairs of elements such as Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc–Re (group 7) possess almost same size. These pair of elements are called ‘chemical twins’. The properties of these elements are also similar. So due to lanthanoid contraction elements of second and third series resemble each other.

(C) **Similarity among lanthanoids:** (1/2)

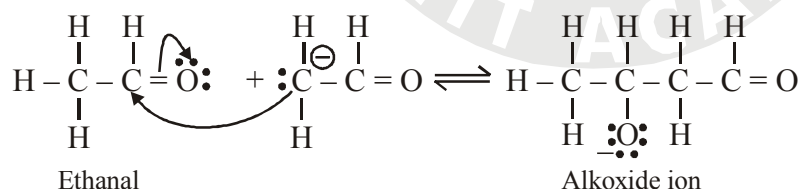
Lanthanoids show very small change in radii so their chemical properties are quite similar. Thus it is very difficult to separate the elements in pure state.

(iii) Aldol condensation involves the following steps :

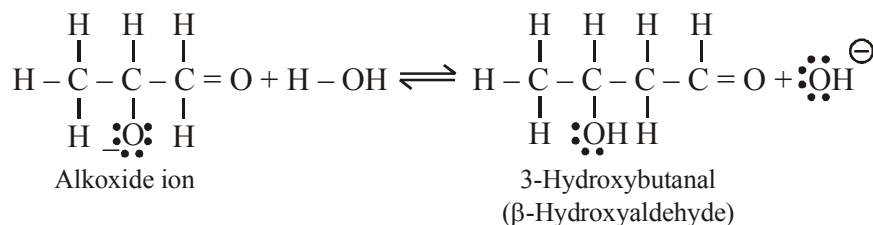
Step 1 : Removal of α -hydrogen atom (which is acidic in nature) from aldehydes and ketones to form a carbanion. (1)



Step 2 : The nucleophilic carbanion or enolate ion attacks the electrophilic carbonyl carbon atom of second molecule of aldehyde to form the alkoxide ion. (1)



Step 3 : The alkoxide ion thus formed, accepts a proton from water, forming aldol and OH^- . (1)



(iv) **Carbohydrate :** Carbohydrates are optically active polyhydroxy aldehydes or polyhydroxy ketones or the compounds that can be hydrolysed to polyhydroxy aldehydes or polyhydroxy ketones. Eg. Glucose, Fructose etc. (1)

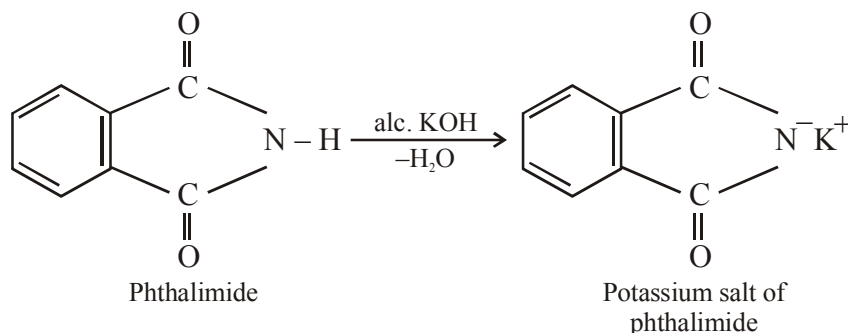
Reducing sugars : Carbohydrates which reduce Fehling’s solution and Tollen’s reagent are referred to as reducing sugars. Eg. Maltose (1)

Non-reducing sugar: Carbohydrates which do not reduce Fehling’s solution and Tollen’s reagent are referred as non-reducing sugars. Eg. Sucrose (1)

Q.8

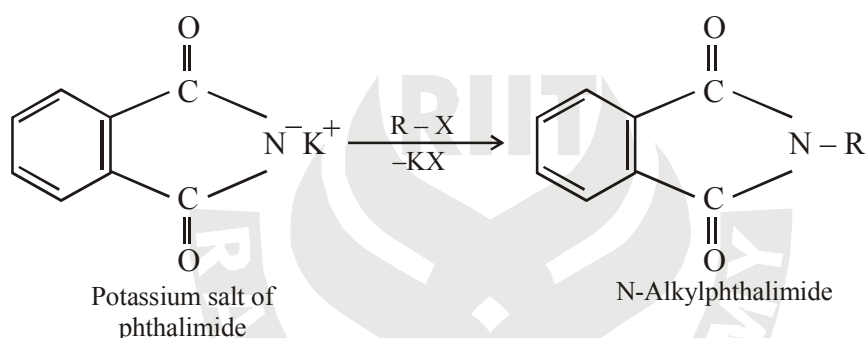
(i) (A) **Gabriel phthalimide synthesis :**

(a) Reaction of phthalimide with ethanolic KOH gives potassium salt of phthalimide. (1)

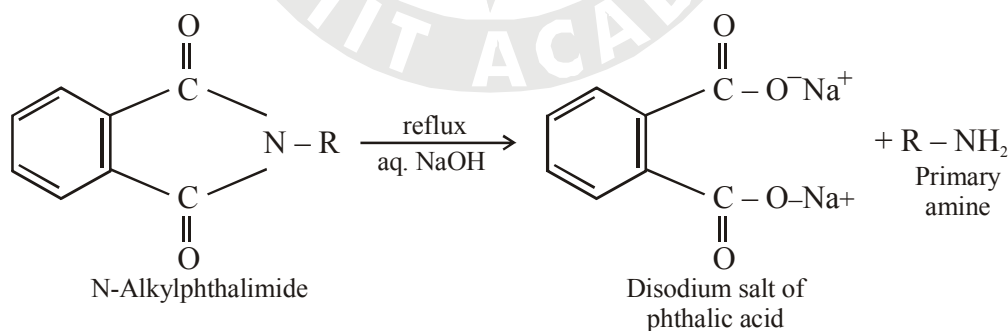


(b) In this step, N – H proton is removed to give imide ion. (1)

(c) Potassium salt of phthalimide is then heated with alkyl halide or benzyl halide.



N-Alkylphthalimide is then hydrolysed (with aqueous NaOH) to give corresponding primary amine.



(d) Over alkylation is avoided so that secondary or tertiary amines are not obtained. (1)

(e) This method is not suitable for preparation of aromatic primary amines (such as aniline, toluidine, etc.) because nucleophilic substitution of aryl halides with phthalimide anion is not possible.

(B) **Biodegradable polymers:** The polymers which are degraded by micro-organisms within a suitable period so that the polymers and their degraded products do not cause any serious effects on the environment are called biodegradable polymers. (1/2)

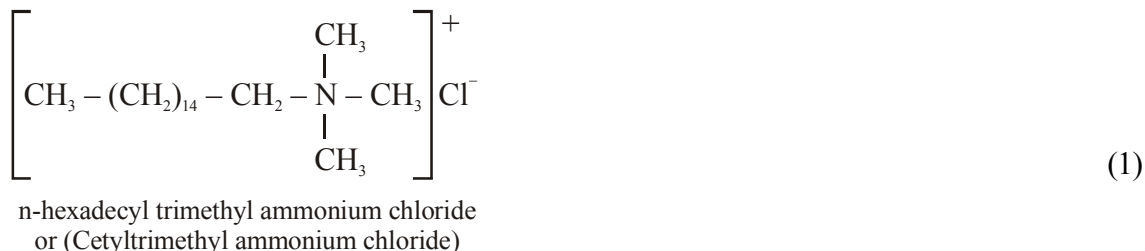
Eg. Nylon-2-nylon-6, Dextron, etc. (1/2)

Non-biodegradable polymers: The polymers are those polymers which are not degraded by micro-organisms. (1/2)

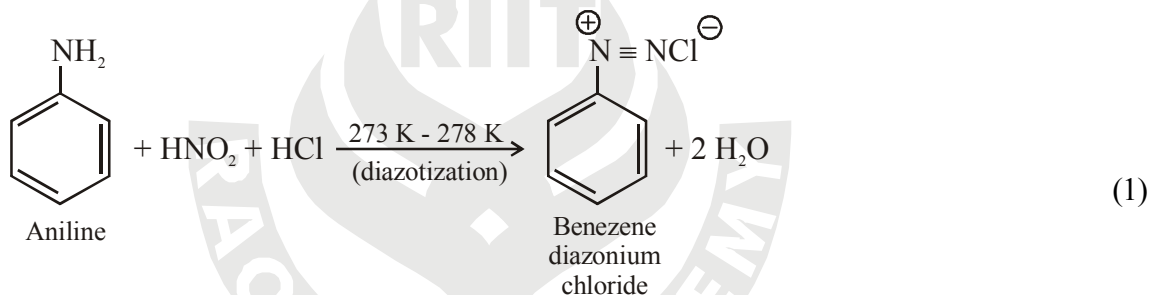
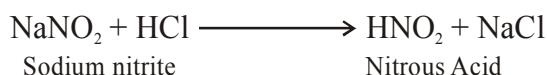
eg. Plastic, Nylon, Terylene etc. (1/2)

(C) Cationic detergents:

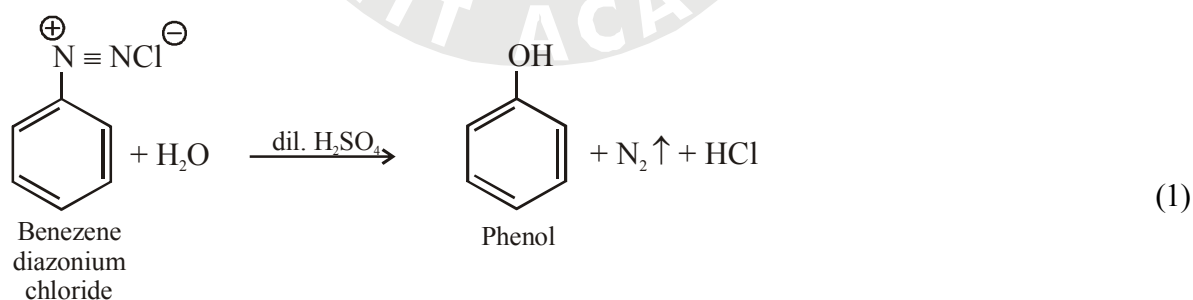
- (a) Cationic detergents are quaternary ammonium salts of amines. (1/2)
- (b) The soluble ends of the chain contains cations. (1/2)
- (c) Anions include chlorides, acetates or bromides and cations include long chain hydrocarbons with positively charged nitrogen atom.



- (ii) (A) (a) **Carbolic acid from Aniline** : When Aniline (or phenyl amine) is treated with nitrous acid (HNO_2) under ice cold condition. (0°C to 5°C) benzene diazonium salt is formed.

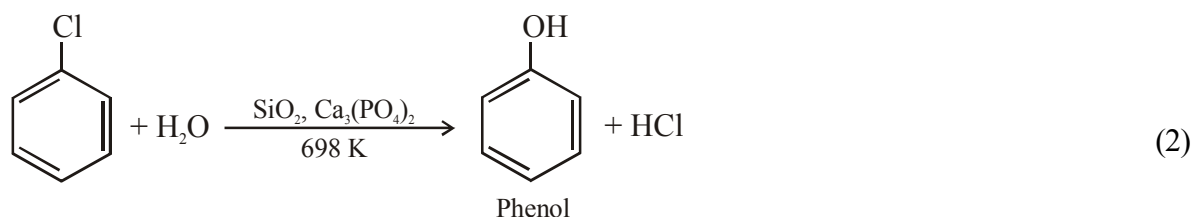


The aqueous solution of benzene diazonium chloride on hydrolysis with dilute sulphuric acid forms phenol.

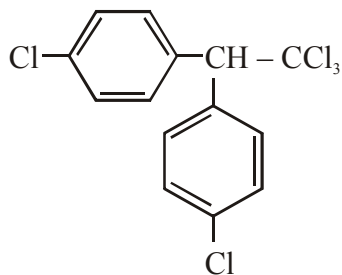


(B) Chlorobenzene and Steam at 698 K (Raschigs process)

When chlorobenzene is treated with steam (H_2O) at 698 K in the presence of $\text{Ca}_3(\text{PO}_4)_2$ or SiO_2 as a catalyst, phenol is obtained.



(C) (a) Structure of DDT



(1)

(b) Effects :

(i) It is not completely biodegradable i.e. it is not very rapidly metabolized by animals. Instead, it gets deposited and store in fatty tissues. It is exists for longtime in soil, plants and animals as well. It produces unforeseen ecological effects. (1/2)

(ii) It is replaced by better and safer insecticide due to ecological problems. (1/2)

(c) Physical properties of carbolic acid :

(1)

(i) Pure phenol is colourless, hygroscopic crystalline solid.

(ii) It has melting point 315 K and boiling point 455 K, the high boiling point of phenol is due to intermolecular H-bonding.

(iii) It is springly soluble in water but completely soluble in alcohol, ether etc.

