

MARKING SCHEME

PRACTICE PAPER - 03

1. (i) (a) $\pi \propto C$, so more the concentration, higher is the osmotic pressure. (1)

(ii) (b) The concentration of BaCl_2 solution is lower, thus solvent (water) moves from the BaCl_2 solution to NaCl solution, when 0.1 M NaCl and 0.005 M BaCl_2 solutions are separated by a semipermeable membrane. (1)

(iii) (a) Osmotic pressure, $\pi = CRT$

Here, $C = 0.2 \text{ M}$

$$R = 0.082 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$$

$$T = (27 + 273)\text{K} = 300 \text{ K}$$

$$\pi = 0.2 \times 0.082 \times 300 = 4.92 \text{ atm} \quad (1)$$

(iv) (d) When a solution of urea (6%) is isotonic with a solution of glucose

$$\pi_{\text{glucose}} = \pi_{\text{urea}}, C_{\text{glucose}} = C_{\text{urea}}$$

$$\therefore \left(\frac{w_g \times 1000}{m_g \times 100} \right) = \left(\frac{w_u \times 1000}{m_u \times 100} \right)$$

where, $w_g = \text{mass of glucose} = x \text{ g}$

$m_g = \text{molecular mass of glucose} = 180 \text{ g mol}^{-1}$

$w_u = \text{mass of urea} = 6 \text{ g}$

$m_u = \text{molecular mass of urea} = 60 \text{ g mol}^{-1}$

$$\therefore \frac{x \times 1000}{180 \times 100} = \frac{6 \times 1000}{60 \times 100} \Rightarrow x = 18 \text{ g}$$

Thus, 18 g of glucose is present in 100 mL of solution.

In other words, 1 M solution of glucose (18 g in 100 mL) is isotonic with 6% solution of urea. (1)

Or

(a) Isotonic solutions have same molar concentration of solute particles in solution. Molar concentration of solute particles in solution are 0.1 M in glucose, $2 \times 0.05 \text{ M}$ in NaCl , 3×0.05 in BaCl_2 and 4×0.1 in AlCl_3 . Therefore, 0.1 M glucose and 0.05 M NaCl solutions are isotonic. (1)

2. (i) (d) Order of basicity of amines in gaseous phase follows the order:

Tertiary amine > secondary amine > primary amine
> NH_3

The basic nature of aliphatic amines increases with increase in the number of alkyl groups (in gaseous phase). Hence, Assertion is incorrect but reason is correct. (1)

(ii) (d) Aliphatic amines are stronger bases than ammonia due to +I-effect of alkyl groups leading to high electron density on the nitrogen atom. Their pK_b values lie in the range of 3 to 4.22. Which is lower than pK_b value of NH_3 , i.e. 4.75. On the other hand, aromatic amines are weaker base than ammonia due to the electron withdrawing nature of the aryl group. (1)

(iii) (d) $MeNH_2$ is the stronger base than $MeOH$ because N is less electronegative than O, lone pair of electrons on N is more easily available for the donation in $MeNH_2$. (1)

(iv) (b) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion. (1)

Aniline exists as resonance hybrid. As a result of resonance, the lone pair of electrons on nitrogen gets delocalised over the benzene ring and thus is less easily available for protonation than in case of cyclohexylamine where no such resonance takes place. (1)

Or

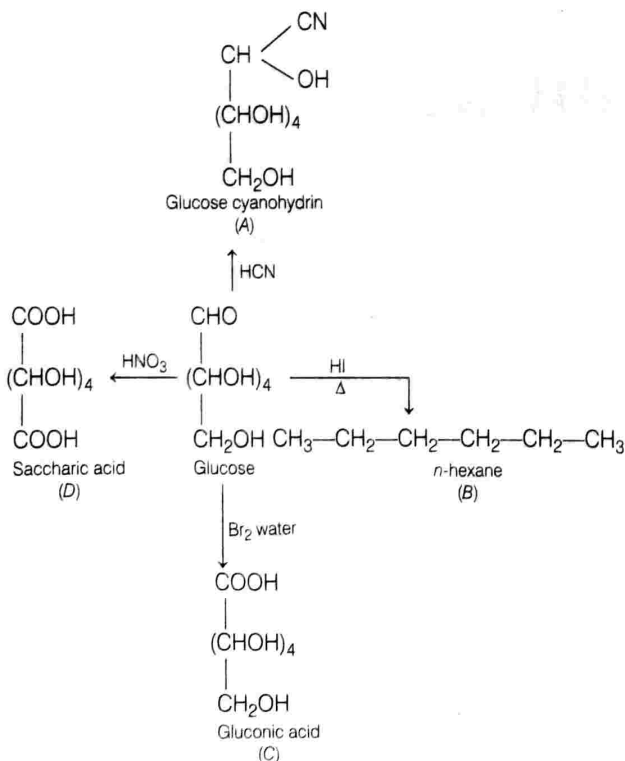
(d) Assertion is incorrect but Reason is correct.

Ammonia is more basic than water. It is because nitrogen being less electronegative than oxygen has a greater tendency to donate electrons. (1)

3. (a) Structure I is β -D-ribose and structure II is β -D-deoxyribose. (1)

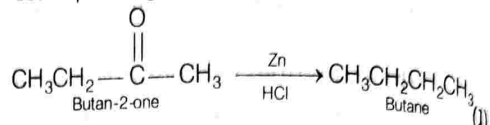
Or

(b) Complete reactions are as follows:



4. (c) The reaction $2NO + Cl_2 \longrightarrow 2NOCl$ represents a third order reaction as its unit of rate constant is $L^2 \text{ mol}^{-2} \text{ s}^{-1}$. (1)

5. (b) Butan-2-one is reduced with Zn and HCl to give corresponding hydrocarbon. (1)



6. (a) Option (a) represents structure of triclinic crystal system as

$$a \neq b \neq c \text{ and } \alpha \neq \beta \neq \gamma \neq 90^\circ$$

Or

(d) There are four body diagonals. Atoms on the body diagonals are not shared by any other unit cell.

$$\text{Contribution by atoms on corners} = 8 \times \frac{1}{8} = 1 \text{ and}$$

$$\text{Contribution by atoms on body diagonal} = 2 \times \frac{1}{2} = 1$$

$$\text{Hence, total number of atoms} = 8 + 1 = 9 \quad (1)$$

7. (c) $\mu = \sqrt{n(n+2)}$ is the correct formula for "spin-only". (1)

8. (b) Since, electronegativity of oxygen is very high, it shows only negative oxidation state as -2 except in the case of OF_2 , where its oxidation state is +2. (1)

Or

(c) Tetrafluorides have sp^3d -hybridisation and trigonal bipyramidal structure in which one of the equatorial positions is occupied by a lone pair of electrons. This geometry is also regarded as see-saw geometry. (1)

9. (b) Acid catalysed hydration of alkenes except ethene leads to the formation of secondary and tertiary alcohol. (1)

10. (b) Two Br, two (en) and one Cr are parts of the complex. Charge on the complex is

$$\left. \begin{array}{l}
 2 (\text{Br}) = -2 \\
 2 (\text{en}) = 0 \\
 1 (\text{Cr}) = +3
 \end{array} \right\} = +1$$

Thus, complex ion is $[\text{Cr}(\text{en})_2\text{Br}_2]^+$. (1)

Or

(a) Magnetic moment, μ is related with number of unpaired electrons as,

$$\begin{array}{l}
 \mu = \sqrt{n(n+2)} \text{ BM} \\
 (1.73)^2 = n(n+2)
 \end{array} \quad (1)$$

On solving, $n = 1$

Thus, the complex compound having one unpaired electron exhibit a magnetic moment of 1.73 BM. (1)

11. (b) Electronegativity of oxygen is very high. It shows only negative oxidation state as -2 except in the case of OF_2 , where oxidation state is +2. (1)

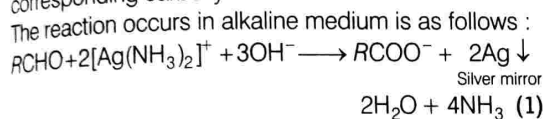
12. (a) In phenols, the —OH group is attached to sp^2 -hybridised carbon atom of an aromatic ring. So, the carbon oxygen bond length (136 pm) in phenol is slightly less than that in methanol. Hence, both Assertion and Reason are correct and Reason is the correct explanation of Assertion. (1)

13. (b) Assertion and Reason both are correct but Reason is not the correct explanation of Assertion.

Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids. Correct reason is due to electron withdrawing nature of C=O group. C—H bond in aldehydes is weak and easily oxidised to the corresponding carboxylic acids even with mild oxidising agent like Fehling's solution and Tollen's reagents. (1)

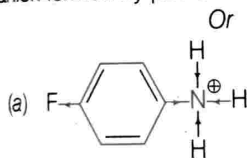
14. (c) Bond cleavage in haloarene is difficult than haloalkane due to partial double bond character in C—Cl bond because of resonance, so it is less reactive towards nucleophilic substitution reaction phenyl carbocation is very unstable. (1)

15. (a) On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's reagent), a bright silver mirror is produced due to the formation of silver metal. The aldehydes are oxidised to corresponding carboxylate anion.

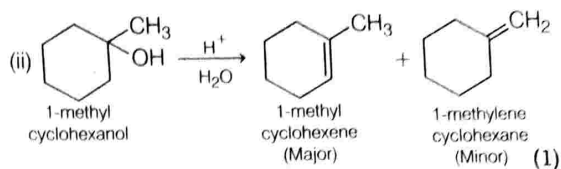
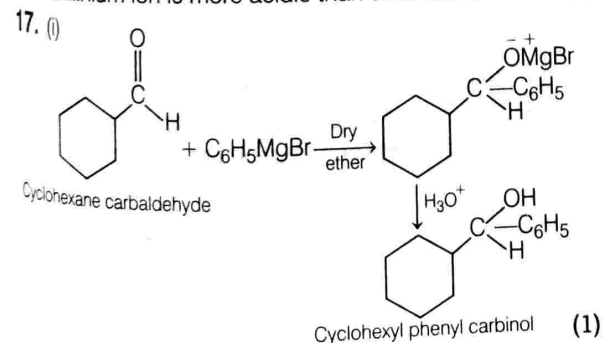


Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

16. (c) Assertion is correct but Reason is incorrect. Aromatic primary amines cannot be prepared by the Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution reaction with the anion formed by phthalimide. (1)



Due to —I-effect of F-atom, it withdraws electron from $\ominus NH_3$ group. As a result, electron density in the N—H bond of *p*-fluoroanilinium ion decreases and hence release of a proton from *p*-fluoroanilinium ion is much more easier than from anilinium ion. Thus, *p*-fluoroanilinium ion is more acidic than anilinium ion. (1)



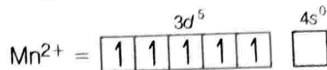
18. Given, conductivity, $\kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}$

Resistance, $R = 1500 \Omega$

\therefore Cell constant = $\kappa \times R$

$$= 0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1} \quad (2)$$

19. (i) The configuration of Mn(II) ion is $3d^5 4s^0$.



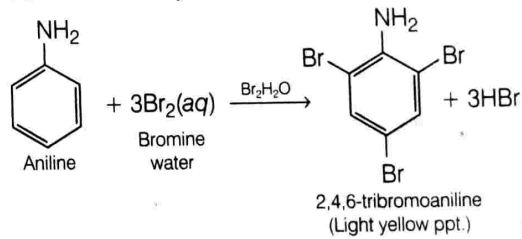
Since, five unpaired electrons are present in $3d$ -orbital of Mn^{2+} ion, thus it shows maximum paramagnetic character among the divalent ions of first transition series of elements. (1)

(ii) Most of the transition metals do not displace hydrogen from dilute acids because most of the transition metals have negative oxidation potential. (1)

Or

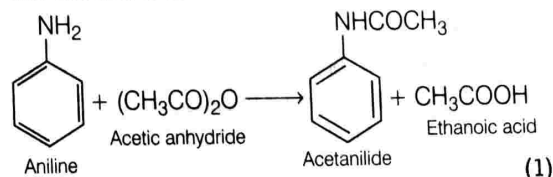
($IE_1 + IE_2$) values of Pt is greater than Ni. Thus, Ni^{2+} compounds are thermodynamically more stable than Pt^{2+} compounds. Also, ($IE_3 + IE_4$) values of Ni is greater than Pt. Thus, Pt^{4+} compounds are thermodynamically more stable than Ni^{4+} compounds. $K_2 [PtCl_6]$ is well known but no such nickel (IV) compound is known. (2)

20. (i) Halogenation reaction takes place when aniline reacts with aqueous solution of bromine water in the absence of catalyst. The reaction is as follows:



(ii) Aniline on reaction with acetic anhydride forms acetanilide.

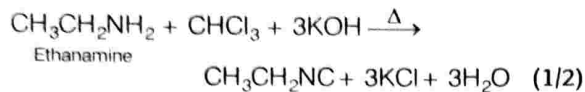
The reaction is as follows :



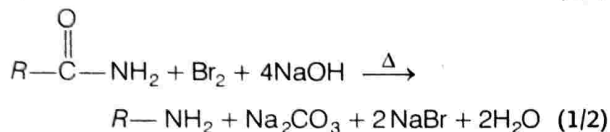
Or

(i) **Carbylamine reaction** Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamine which are foul smelling substances.

This reaction is known as carbylamine reaction. This reaction is used as a test for primary amine. (1/2)

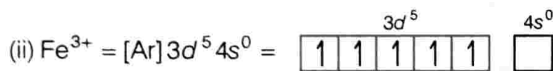


- (ii) **Hofmann bromamide reaction** It is a method used for the preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. The amines so formed contains one carbon less than that present in the parent amide. (1/2)

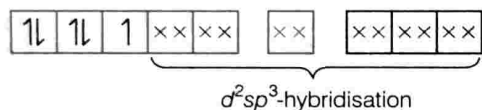
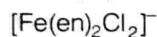


21. (i) Let the oxidation number of iron (Fe) be x in $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$.

$$x + 0 + 2(-1) = +1; x = +3. \quad (1)$$



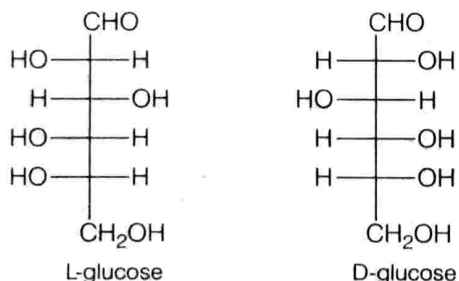
Fe^{3+} (in presence of ligand)



d^2sp^3 -hybridisation (six hybrid orbitals) (1)

Shape-Octahedral.

22. (i) The Fischer projection of D-glucose and L-glucose are as follows:

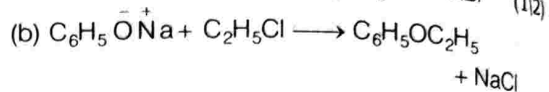
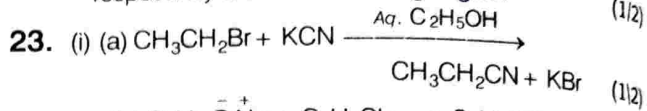


D-glucose reduces Tollen's reagent to metallic silver and forms gluconic acid. (1)

- (ii) Sucrose possess eight —OH groups, while glucose has five —OH groups which forms intermolecular H-bonds with water because of this extensive intermolecular hydrogen bonding.

Hence, sucrose and glucose are soluble in water. In contrast, benzene or cyclohexane is insoluble in water because of the absence of —OH groups, and thus they do not form H-bonds with water. (1/2)

- (iii) Carbohydrates which reduce Fehling's solution or Tollen's reagent to form a red precipitate of Cu_2O or a silver mirror respectively are called reducing sugars. (1/2)

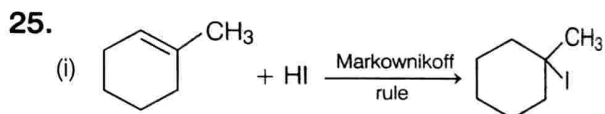


- (ii) The correct increasing order of nucleophilic substitution reactions is $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$. Because C—X bond have bond dissociation energy in the sequence $\text{C—F} > \text{C—Cl} > \text{C—Br} > \text{C—I}$. (1)

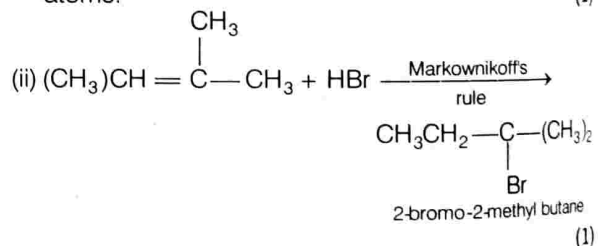
24. Ethanol can be distinguished from phenol by the following tests:

(i) **Coupling reaction** Phenols react with diazonium salts in weakly basic solution to form yellow coloured azo dyes but ethanol do not react. (1)



(ii) **Bromine water test** Phenol on reaction with bromine water gives a white ppt of 2, 4, 6-tribromophenol but ethanol do not. (1)




According to Markownkioff's rule, iodine will add to the carbon atom having less number of hydrogen atoms. (1)




Or

- (i)  is a tertiary haloalkane and  is a secondary haloalkane. For a $\text{S}_\text{N}1$ reaction, the rate of reaction follows the order :

Primary < Secondary < Tertiary

Therefore,  reacts faster because it is a tertiary

haloalkane. The  is a secondary haloalkane. (1)

- (ii) Reaction of alkyl chloride with aqueous KOH is a **nucleophilic substitution reaction** in which chlorine atom goes out as Cl^- and is replaced by a stronger nucleophile OH^- by $\text{S}_\text{N}1$ mechanism producing an alcohol.

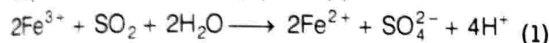
The reaction of alkyl chloride with alcoholic KOH is a **elimination reaction**. During this reaction, one molecule of HCl is removed to produce an alkene. (1)

26. (i) (a) Oxygen molecules are held together by weak van der Waals' forces because of small size and high electronegativity of oxygen. These Vander, Waal's forces of attraction can be easily overcome by collisions of the molecules at room temperature, therefore, O_2 exists as a gas.

Due to catenation, sulphur forms S_8 molecules having eight membered puckered ring. Because of its bigger size, the forces of attraction holding S_8 molecules much stronger which cannot be overcome by collisions of molecules. Hence, sulphur is a solid. (1)

- (b) Fluorine atom is smaller in size, so six F^- ions can surround a sulphur atom. The case is not so with chlorine atom due to its large size. So, SF_6 is known but SCl_6 is not known due to interionic repulsion between larger Cl^- ions. (1)

- (ii) SO_2 acts as a reducing agent and hence reduces an aqueous solution of Fe(III) to Fe(II).



27. **Step I** Calculation of molecular masses of compounds AB_2 and AB_4 .

For compound AB_2 ,

$$w_2(\text{solute } AB_2) = 1g,$$

$$w(C_6H_6) = 20g; \Delta T_f = 2.3K$$

$$K_f = 5.1K \text{ kg mol}^{-1}$$

$$M_{(AB_2)} = \frac{1000 \times K_f \times w_2}{\Delta T_f \times w(C_6H_6)}$$

$$= \frac{(5.1K \text{ kg mol}^{-1}) \times (1g) \times 1000}{(2.3K) \times (20g)}$$

$$= 110.87g \text{ mol}^{-1}$$

For compound AB_4 ,

$$w_2 = 1g, w_1 = 20g, \Delta T_f = 1.3K$$

$$K_f = 5.1K \text{ kg mol}^{-1}$$

$$M_{AB_4} = \frac{(5.1K \text{ kg mol}^{-1}) \times 1000 \times (1g)}{(1.3K) \times (20g)}$$

$$= 196.15g \text{ mol}^{-1}$$

(1½)

Step II Calculation of the atomic masses of elements A and B

Let the atomic mass of element A be a.

Let the atomic mass of element B be b.

Molecular mass of $AB_2 = a + 2b$

Molecular mass of $AB_4 = a + 4b$

According to the available data,

$$a + 2b = 110.87$$

...(i)

$$a + 4b = 196.15$$

...(ii)

On subtracting Eq. (i) from Eq. (ii),

$$a + 4b - a - 2b = 196.15 - 110.87$$

$$2b = 85.28$$

$$\Rightarrow b = \frac{85.28}{2} = 42.64$$

On substituting the value of b in Eq. (i)

$$a + 2 \times 42.64 = 110.87$$

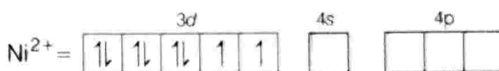
$$a + 85.28 = 110.87$$

$$a = 110.87 - 85.28 = 25.59$$

Thus, atomic mass of element A is $25.59g \text{ mol}^{-1}$ and

atomic mass of element B is $42.64g \text{ mol}^{-1}$. (1½)

28. The configuration of Ni^{2+} ion is $[Ar] 3d^8 4s^0$.



In $[Ni(H_2O)_6]^{2+}$, H_2O molecules are weak field ligands, they do not cause electron pairing. As a result, the complex has two unpaired electrons. Thus, $d-d$ transition takes place due to absorption of radiation corresponding to red light and the emission of complementary green colour occurs.

Hence, it is green. In $[Ni(CN)_4]^{2-}$, CN^- are strong ligands so in the presence of CN^- ions, the two unpaired electrons in the $3d$ -orbital pair up. Hence, there is no unpaired electron and no transition. Hence, it is colourless. (3)

Or

Hexaammine chromium (III) ion, $[Cr(NH_3)_6]^{3+}$ ion

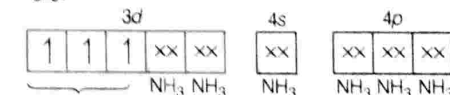
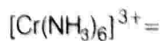
Oxidation state of Cr = +3

$${}_{24}Cr = [Ar] 3d^5 4s^1$$

$$Cr^{3+} = [Ar] 3d^3$$

Cr^{3+} provides six empty orbitals to accommodate six electron pairs from six NH_3 molecules. It involves d^2sp^3 -hybridisation and hence, octahedral.

It is paramagnetic due to the presence of three unpaired electrons. (1)

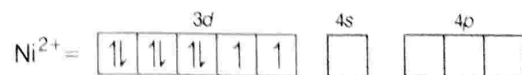


Three unpaired electron

d^2sp^3 -hybridisation

Tetracyanonickelate (II) ion, $[Ni(CN)_4]^{2-}$

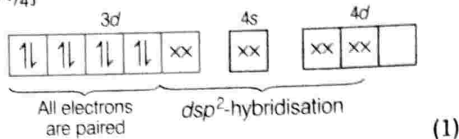
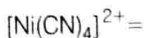
$$Ni = [Ar] 3d^8 4s^2, Ni^{2+} = [Ar] 3d^8$$



(1)

(CN⁻ being strong field ligand causes pairing of 3d electrons thus, one of the 3d-orbital becomes empty for CN⁻ ion.)

Unpaired electron is not present, so it is diamagnetic.



29. Given, density, $d = 112 \text{ g cm}^{-3}$

edge length, $a = 4 \times 10^{-8} \text{ cm}$

for fcc, $Z = 4$

$$\therefore d = \frac{Z \times M}{a^3 \times N_A}$$

$$M = \frac{d \times a^3 \times N_A}{Z} \quad \dots (i) \quad (1)$$

$$= \frac{112 \text{ g cm}^{-3} \times (4 \times 10^{-8} \text{ cm})^3 \times 6.022 \times 10^{23} \text{ mol}^{-1}}{4} = 107.9 \approx 108 \text{ g mol}^{-1} \quad (2)$$

30. (i) The air becomes dry when passed over silica gel because silica gel adsorbs moisture present in the air. (1)

(ii) Colloidal medicines are more effective in the treatment of diseases because of large surface area and therefore easily assimilated. (1)

(iii) Adsorption is an exothermic process, so ΔH is always negative and ΔS is also negative because after adsorption of gas, entropy decreases. (1)

Or

(i) Artificial rain occurs when oppositely charged clouds meet one another. Since, clouds are colloidal in nature and usually carry similar charge that repels them. Spray of salts (electrolytes) neutralises the charge on cloud and clouds come close together leading to rain. Sometimes, electrification is also used for this purpose. (1)

(ii) Eosin is adsorbed on the surface of silver halide and get precipitated making it coloured. (1)

(iii) In lyophilic colloids, dispersed phase particles have strong affinity with dispersion medium. So, these are more stable. (1)

31. (i) Let, $a = 0.8 \text{ M}$, $a - x = 0.4 \text{ M}$, $t = 15 \text{ min}$

For first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{15} \log \frac{0.8}{0.4} = 0.462 \text{ min}^{-1}$$

\therefore Time taken for 0.1 M to 0.025 M can be calculated as

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{0.462} \log \frac{0.1}{0.025} = 30 \text{ min}$$

(ii) If a first order reaction is 60% complete in 100 min (2)

Let, $[x]_0 = 100 \text{ M}$, $[x]_{60\%} = 100 - 60 = 40 \text{ M}$

and $t = 100 \text{ min}$

$$k = \frac{2.303}{t} \log \frac{x_0}{x} = \frac{2.303}{100} \log \frac{100}{40} = 0.02303 \log 2.5 = 0.02303 \times 0.397 = 0.009 \text{ min}^{-1}$$

Time taken to complete 90% reaction = ?

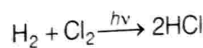
$[x]_0 = 100 \text{ M}$, $[x]_{90\%} = 100 - 90 = 10 \text{ M}$

$k = 0.009 \text{ min}^{-1}$

$$t = \frac{2.303}{k} \log \frac{x_0}{x} = \frac{2.303}{0.009} \log \frac{100}{10} = 255.8 \log 10 = 255.8 \text{ min}$$

Or

(i) For a reaction,



Rate = k , suggests that, the reaction is of zero order

(a) Further, the molecularity of a given reaction is 2 as two molecules are participating in the reaction,

Hence, order = zero and molecularity = two

(b) The unit of k for zero order reaction is equal to the rate of a reaction which is $\text{mol L}^{-1}\text{s}^{-1}$. Hence, the unit of k for the given reaction is $\text{mol L}^{-1}\text{s}^{-1}$ (2)

(ii) A reaction is second order in A and first order in B

(a) Differential rate equation,

$$\text{Rate} = -\frac{d[R]}{dt} = k[A]^2[B]$$

(b) When the concentration of A is increased three i.e. 3A, then

$$\text{Rate} = k[3A]^2[B] = 9k[A]^2[B] = 9(\text{rate})$$

This shows that rate will increase 9 times to the rate.

(c) When concentration of both A and B is doubled.

$$\text{Rate} = k[2A]^2[2B] = 8k[A]^2[B] = 8(\text{rate})$$

This shows that rate will increase 8 times to the rate. (3)

32. (i) The electronic configuration of Hg(l) is $[\text{Xe}]4f^{14}5d^{10}6s^1$. It has one unpaired electron in the valence 6s-subshell. It is paramagnetic but actually Hg(l) compounds are diamagnetic. This change can be explaining by assuming that the singly filled

6s-orbitals of two Hg⁺ ion overlap to form Hg—Hg covalent bond. Therefore, Hg⁺ ion exists as dimeric species, i.e. Hg₂²⁺. On the other hand, Cu(I) ion has electronic configuration [Ar]3d¹⁰. It has no unpaired electron to form dimeric Cu₂²⁺ species and therefore, it exists as Cu⁺ ion. (2)

(ii) (a) Transition metal compounds are paramagnetic in nature due to the presence of unpaired electrons in d-subshells. (1)

(b) The compounds in which small atoms like H, C, N, etc., occupy interstitial sites in the crystal lattice are called interstitial compounds.

These compounds are well known for transition metals because small atoms can easily occupy the positions in the voids presents in the crystal lattices of transition metals. (1)

(c) Zinc (Zn) has completely filled d orbitals, so it does not take part in bonding.

Thus, metallic bond is weaker than the other elements of the series. In other elements of the series, the electrons of d-orbitals are involved in the formation of metallic bonds. So, high enthalpy of atomisation is observed. (1)

Or

(i) (a) When Cu²⁺ ion is treated with KI, it produces white precipitate Cu₂I₂ in the final product.



(In this reaction, CuI₂ is formed which being unstable dissociate into Cu₂I₂ and I₂). (1)

(b) This problem is based on concept of Fajan's rule. As the oxidation state increases, size of the ion of transition element decreases. As per Fajan's rule, as the size of metal ion decreases, covalent character of the bond between metal and halide formed increases. (1)

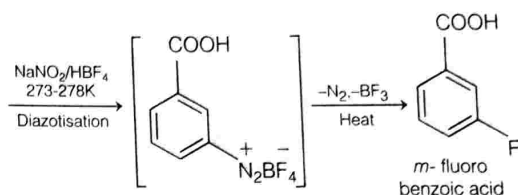
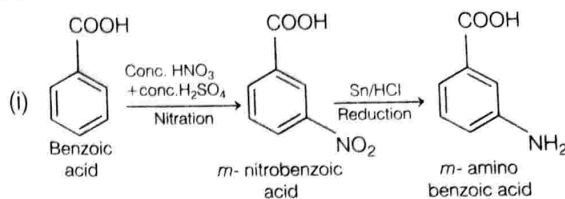
(ii) (a) Mn³⁺ / Mn²⁺ has large positive E° value. Hence, Mn³⁺ can be easily reduced to Mn²⁺ because Mn²⁺ has half-filled electronic configuration, so it is stable and Mn²⁺ is least stable.

Therefore, it is a good oxidising agent. (1)

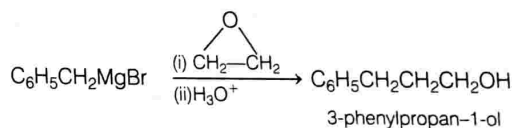
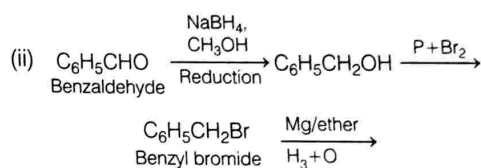
(b) There is decreasing negative electrode potentials of M²⁺ / M in the first transition series due to increase in the sum IE₁ + IE₂. It shows that in general, the stability of +2 oxidation state decreases from left to right (exceptions are Mn and Zn in which the greater stability of +2 state for Mn is due to half-filled d subshell (d⁵) in Mn²⁺ and that of Zn is due to completely filled d-subshell (d¹⁰) in Zn²⁺) (1)

(c) It is because oxygen can form multiple bonds, whereas fluorine can only form single bonds with metals. (1)

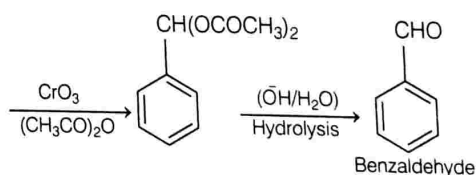
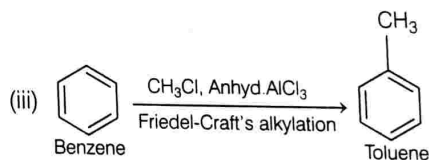
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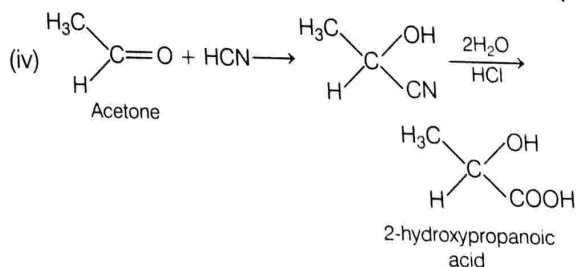
(1)



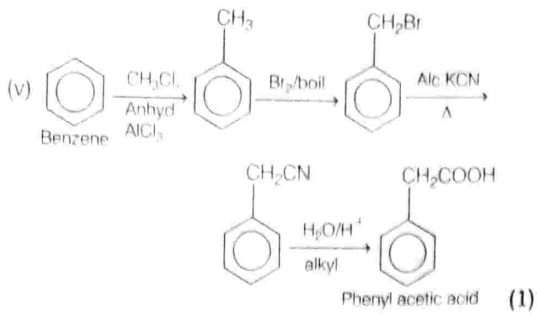
(1)



(1)



(1)



Or

