Chemistry 2012 (Outside Delhi) SET I

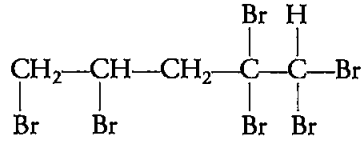
Time allowed : 3 hours **Maximum marks : 70**

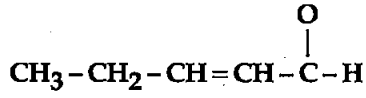
1. **How may the conductivity of an intrinsic semiconductor be increased ?**** [1]

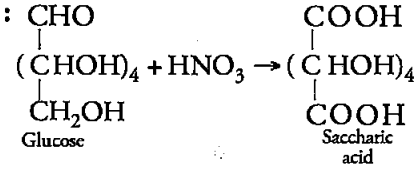
2. **Define 'peptization'.** [1]
Answer : The process of conversion of freshly prepared precipitate into a colloidal solution by adding suitable electrolyte is called peptization.

3. **How is copper extracted from a low grade ore of it ?** [1]
Answer : Copper from its low grade ore is leached out using acid or bacteria and then Cu^{2+} ions in the solution are reduced to copper by treating it with Hydrogen or Iron. This method is called hydrometallurgy.

4. **Which is a stronger reducing agent, SbH_3 or BiH_3, and why ?**** [1]

5. **What happens when bromine attacks**
$CH_2 = CH - CH_2 - C \equiv CH$? [1]
Answer :
$CH_2{=}CHCH_2C^{\circ}CH + Br_2 \rightarrow$
$CH_2{=}CH{-}CH_2{-}C(Br){=}CH{-}Br$
And if Br_2 is in excess then


6. **Write the IUPAC name of the following :** [1]

Answer : Pent-2-enal

7. **Write the structure of the product obtained when glucose is oxidised with nitric acid.** [1]
Answer :

Glucose — Saccharic acid

8. **Differentiate between disinfectants and antiseptics.** [1]
Answer : Antiseptics are used on living tissues to kill or prevent the growth of microorganisms. It does not cause any harm to the living tissues *e.g.* 0.2% solution of phenol.
Disinfectants are used on non-living objects to kill the micro-organisms. They are harmful to the living tissues and hence, cannot be applied to the skin *e.g.* 1% solution of phenol.
$M = 0.2085\ S\ cm^{-1}$

**** Answer is not given due to change in present syllabus.**

9. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity. [2]

OR

The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.

Answer : $CG^* = k$

Where, C = conductance, G^* = cell constant, k = conductivity

$$G^* \times \frac{1}{R} k \Rightarrow G^* = Rk$$

$$\therefore \Lambda_m = \frac{k \times 1000}{M} Scm^2 mol^{-1}$$

OR

Given : M = 1.5 M

$\Lambda_m = 138.9\ S\ cm^2\ mol^{-1}$

$$\Lambda_m = \frac{1000K}{M}$$

$$M = \frac{k.\Lambda_m}{1000} = \frac{1.5 \times 138.9}{1000}$$

$M = 0.2085\ S\ cm^{-1}$

10. A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (ii) reduced to half ? [2]

Answer : (i) Rate increases by four times,

$R' = 2R \Rightarrow r = k[2R]^2 = 4kR^2$

(ii) Rate is reduced by ¼ times,

$$R' = \frac{1}{2}R \Rightarrow r = k\left[\frac{R}{2}\right]^2 = \frac{k}{4}R^2$$

11. Which methods are usually employed for purifying the following metals : [2]

(i) Nickel, (ii) Germanium.

Mention the principle behind each one of them.

Answer : (i) Mond's Process : In this method Nickel form volatile complex with Co which decomposes on heating to give pure nickel.

(ii) Zone Refining : It is based on the principle that the impurities are more soluble in the molten state than in the solid state of metal.

12. Explain the following facts giving appropriate reason in each case : [2]

(i) NF_3 is an exothermic compound whereas NCl_3 is not.

(ii) All the bond in SF_4 are not equivalent.

Answer : (i) The bond energy of F-F bond is lower that of N-F bond So NF_3 is an exothermic compound whereas bond energy of Cl-Cl bond is higher than N-Cl bond so NCl_3 is an endothermic compound.

(ii) SF_4 has see-saw structure with bond pairs at two equatorial and two axial positions. Hence, all the bonds in SF_4 are not equivalent.

13. Complete the following chemical reaction equations : [2]

(i) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow$

(ii) $MnO_4^- + NO_2^- + H^+ \longrightarrow$

Answer :

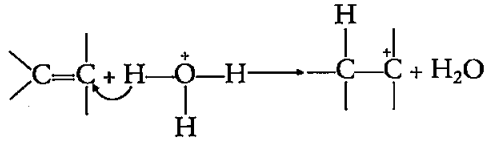
(i) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

(ii)

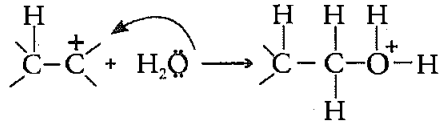
$2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

14. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. [2]

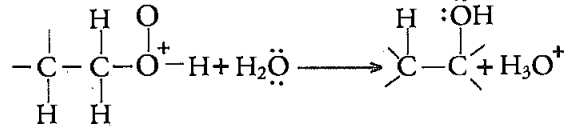
Answer : Step1 : Carbocation is formed due to electrophilic attack by H_3O^+.



Step 2 : Nucleophilic water attacks the carbocation.



Step 3 : Deprotonation to form an alcohol



15. Explain the following behaviours : [2]

(i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

(ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Answer : (i) Due to the formation of hydrogen bonds by alcohols with water molecules.

(ii) The phenoxide ion is more stable for *o*-nitrophenol as nitro group is electron withdrawing due to resonance while methoxy group is electron donating via resonance.

16. Describe the following giving the relevant chemical equation in each case : [2]

(i) Carbylamine reaction

(ii) Hofmann's bromamide reaction.

Answer : (i) Carbylamine Reaction : When

aliphatic and aromatic primary amines are heated with chloroform and ethanolic KOH solution, they form isocyanides or carbylamines which are foul smelling substances.

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

(ii) Hofmann's Bromamide Reaction : In this reaction, primary amines are prepared by treating an amide with Br_2 in an aqueous or alcoholic solution of NaOH

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

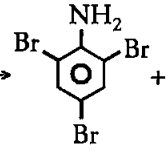
17. Complete the following reaction equations : [2]

(i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(ii) $C_6H_5NH_2 + Br_2(aq.) \longrightarrow$

Answer :

(i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_2PO_3 + HCl$

(ii) $C_6H_5NH_2 + 3Br_{2(aq)} \rightarrow$  $+ 3HBr$

18. What are food preservatives? Name two such substances. [2]

Answer : Chemicals used to prevent spoilage of food by preventing growth of microorganisms like bacteria, fungus etc are called food preservatives. Sodium benzoate, nitrogen gas are two such substances which are used as food preservatives.

19. Copper crystallizes with face centred cubic unit cell. If the radius of copper atom is 127.8 pm, Calculate the density of copper metal. [3]
(Atomic mass of Cu = 63.55 u and Avogadro's number $N_A = 6.02 \times 10^{23}$ mol^{-1})**

OR

Iron has a body centred cubic unit cell with the cell dimension of 286.65 pm. Density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number. (Atomic mass of Fe = 56.0 u)**

20. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. [3]

Answer :

$A = \pi r^2 = 3.14 \times (0.5)^2 = 0.785$ cm^2, $l = 50$ cm

$$R = \frac{\rho l}{A} \quad \rho = \frac{AR}{l} = \frac{5.55\times10^{-3}\times0.785}{50}$$

$$\rho = 87.18\ \Omega\ \text{cm}$$

$$\text{Conductivity, } K = \frac{1}{\rho} = 0.01147\ \text{S cm}^{-1}$$

$$\text{Molar Conductivity} = \frac{1000\times K}{C} = \frac{0.01147\times1000}{0.05}$$

$$\Lambda_m = 229.4\ \text{S cm}^2\text{mol}^{-1}$$

21. The reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0×10^{-5}. Suppose in a case $[N_2] = 0.80$ mol L^{-1} and $[O_2] = 0.20$ mol L^{-1} before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K. [3]

Answer :

	$N_2(g)$	+ $O_2(g)$	$\rightleftharpoons$ $2NO(g)$
Initial conc.	0.80	0.20	0
at equilibrium	$0.80 - x$	$0.20 - x$	$2x$
Initial conc. at : equilibrium	$0.80-x$	0.80	$0.20\ 2x$

$$K = \frac{[NO]^2}{[O_2][N_2]} = \frac{(2x)^2}{(0.8-x)(0.2-x)} = 10^{-5}$$

$$\Rightarrow \quad \frac{(4x)^2}{0.16 - 1x + x^2} = 10^5$$

$$\Rightarrow \quad 400000x^3 = x^2 - x + 0.16$$

$$\Rightarrow 399999\,x^2 + x - 0.16 = 0$$

$$b^2 - 4ac = (1)^2 - 4(399999)(-0.16)$$

$$= 1 + 255999.36 = 256000.36$$

$$\Rightarrow \quad \sqrt{b^2 - 4ac} = \sqrt{256000.36} = 505.96$$

$$x = \frac{-1 \pm 505.96}{2\times399999} = \frac{504.96}{2\times399999}$$

$$= 0.63 \times 10^{-3}$$

$[NO] = 2x = 2 \times 0.63 \times 10^{-3} = 1.26 \times 10^{-3}$ mol/litre

22. Explain the following terms giving a suitable example for each : [3]

(i) Aerosol, (ii) Emulsion, (iii) Micelle.

Answer : (i) An aerosol is a colloid in which dispersed phase is a solid and dispersion medium is a gas *eg.*, Dust, smoke.

(ii) Emulsion is a colloid solution in which both the dispersed phase and dispersion medium are in liquid state. *eg.*, Milk and cod liver oil.

(iii) They are associated colloids showing colloidal behaviour at high concentration and

**Answer is not given due to change in present syllabus.

strong electrolytes at low concentration. *e.g.*, Soap.

23. How would you account for the following : [3]

(i) Among lanthanoids, Ln (III) compounds are predominant. However, occasionally in solution or in solid compounds, +2 and +4 ions are also obtained.

(ii) The $E^\circ_{m^{2+}/m}$ for copper is positive (0.34 V). Copper is the only metal in the first series of transition elements showing this behaviour.

(iii) The metallic radii of the third (5*d*) series of transition metals are nearly the same as those of the corresponding members of the second series.

Answer : (i) Some lanthanoid show +2 and +4 oxidation states in ionic solutions or solid components due to the extra stability that arises because of empty half-filled or fully filled 4*f*-subshell.

(ii) This is because copper has high enthalpy of atomization and low enthalpy of hydration. Hence, $E^\circ_{Cu^{2+}/Cu}$ is positive.

(iii) This is because of lanthanoid contraction the metallic radii of the third (5*d*) series of transition metals are nearly the same as those of the corresponding members of the second series.

24. Name the following coordination entities and draw the structures of their steroisomers : [3]

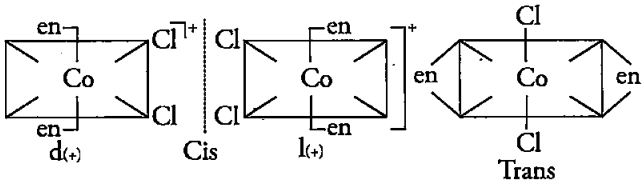
(i) $[Co(en)_2Cl_2]^+$ (en = ethan-1, 2-diamine)

(ii) $[Cr(C_2O_4)_3]^{3-}$

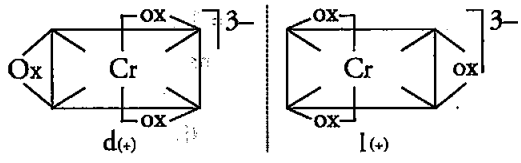
(iii) $[Co(NH_3)_3Cl_3]$

(Atomic numbers Cr = 24, Co = 27)

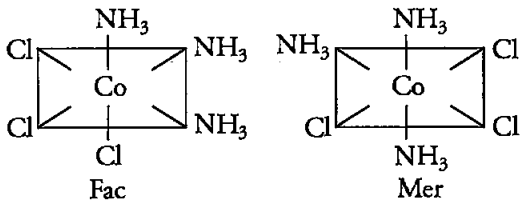
Answer : (i) $[Co(en)_2Cl_2]^+$ dichloridobis (ethan-1,2 diamine) cobalt **(III)** ion



(ii) $[Cr(C_2O_4)_3]^{3-}$: Trioxalatochromate **(III)** ion



(iii) $[Co(NH_3)_3Cl_3]$ triamminetrichloridocobalt **(III)**



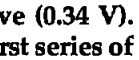
25. Answer the following questions : [3]

(i) What is meant by chirality of a compound ? Give an example.

(ii) Which one of the following compounds is more easily hydrolyzed by KOH and why ?

$CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$

(iii) Which one undergoes S_N2 substitution reaction faster and why ?



Answer : (i) Chirality is the property of a molecule to have non-superimposable mirror images. These molecules contain one asymmetric carbon atom.

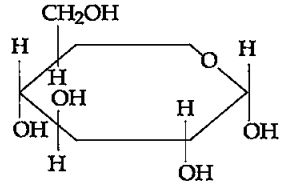
e.g., Butan - 2- ol

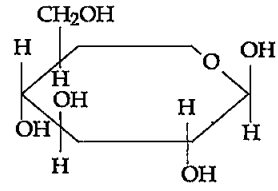
(ii) $CH_3CHClCH_2CH_3$ is more easily hydrolyzed due to the formation of more stable secondary carbocation.

(iii) $CH_3CH_2CH_2Cl$ undergoes S_N2 substitution reaction faster because it is a better leaving group due to its large size and less electronegativity.

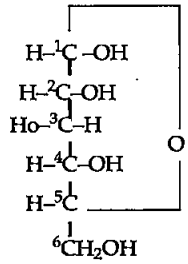
26. What is essentially the difference between α-glucose and β-glucose ? What is meant by pyranose structure of glucose ? [3]

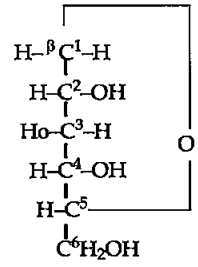
Answer : α-glucose and α-glucose are two cyclic hemiacetal forms of glucose which differ only in the configuration of hydroxyl group (–OH) at anomeric carbon. Such isomers are called anomers. The six-membered cyclic structure of glucose is called pyranose structure.





Pyranose Structure of Glucose : The six membered ring contains oxygen atom because of its resemblance with pyran it is called pyranose form.





27. Differentiate between thermoplastic and thermosetting polymers. Give one example of each. [3]

Answer : Thermoplastic Polymers : These

polymers do not have cross-links between their chains and hence can be reshaped upon heating eg. Polyethylene, Polypropene etc.

Thermosetting Polymers : These polymers have cross-links between their chains and hence cannot be reshaped upon heating. *eg.* Bakelite, Melamine etc.

28. (a) Define the following terms : [5]

(i) Mole fraction

(ii) Ideal solution.

(b) 15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at –0.34 °C. What is the molar mass of this material ? (K_f for water = 1.86 K kg mol^{-1})

OR

(a) Explain the following :

(i) Henry's law about dissolution of a gas in a liquid.

(ii) Boiling point elevation constant for a solvent.

(b) A solution of glycerol ($C_3H_8O_3$) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42°C. What mass of glycerol was dissolved to make this solution ? (K_b for water = 0.512 K kg mol^{-1}).

Answer : (a) (i) The ratio of number of moles of a solute (components of a mixture) to the total number of moles in the mixture is called mole fraction $x_A = \frac{n_A}{n_A + n_B}$ or $x_B = \frac{n_B}{n_A + n_B}$

(ii) A solution that obey's Raoult's law at all temperature and concentration is called an ideal solution.

(b) Given : $W_2 = 15.0$ g, $\Delta T_f = 0.34$°C

$W_1 = 450$ g, $K_f = 1.86$ K kg mol^{-1}

from the formula, $DT_f = \frac{1000.K_f \times W_2}{W_1 \times M_2}$

$$M_2 = \frac{1000\ K_f \times W_2}{\Delta T_f \times W_1} = \frac{1000 \times 1.86 \times 15}{0.34 \times 450}$$

$M_2 = 182.35$ g/mol

OR

(a)(i) Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas. *i.e.*, $p = K_H x$

(ii) The boiling point elevation constant for a solvent is defined as the elevation in boiling point when the molality of the solution is unity.

(b) Given :

$W_1 = 500$ g

$K_b = 0.512$ K kg mol^{-1}

$\Delta T_b = (100.42 - 100)$°C

$= 0.42$°C

$$\Delta T_b = \frac{1000 \times K_b \times W_2}{W_1 \times W_2}$$

$$W_2 = \frac{\Delta T_b \times W_1 \times M_2}{100 \times Kb} = \frac{0.42 \times 500 \times 92}{1000 \times 0.512}$$

$W_2 = 37.7$ g

29. (a) Draw the molecular structures of the following compounds : [2,3]

(i) N_2O_5 **(ii) $XeOF_4$.**

(b) Explain the following observations :

(i) Sulphur has a greater tendency for catenation than oxygen.

(ii) I-Cl is more reactive than I_2.

(iii) Despite lower value of its electron gain enthalpy with negative sign, fluorine (F_2) is a stronger oxidizing agent than Cl_2.

OR

(a) Complete the following chemical equations :

(i) $Cu + HNO_3$ (dilute) →

(ii) $XeF_4 + O_2F_2$ →

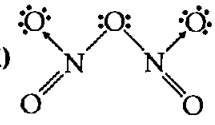
(b) Explain the following observations :

(i) Phosphorus has greater tendency for catenation than nitrogen.

(ii) Oxygen is a gas but sulphur a solid.

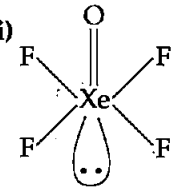
(iii) The halogens are coloured. Why ?

Answer : (a) (i)



N_2O_5

(ii)



$XeOF_4$

(b) (i) Due to strong S—S bond and less interelectronic repulsion, sulphur has greater tendency for catenation.

(ii) I—Cl bond is polar and hence more reactive compound to I_2 in which I—I bond is non-polar.

(iii) Due to high electronegativity and small size of fluorine, it acts as a stronger oxidizing agent.

OR

(a) (i) $3Cu + 8HNO_3$ (dil.) $\longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(ii) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

(b)(i) Catenation (*i.e.* linking of atoms of the same kind with one another) is related to the atom-atom bond energy. Greater the atom-atom bond energy, greater is the catenation. Because of low N—N bond energy (163.8 kJ mol^{-1}) nitrogen shows little tendency for catenation. P—P bond energy (201×10^{-6} kJ/mol) is quite high, hence, it shows more tendency for catenation than nitrogen.

(ii) Oxygen forms $p\pi - p\pi$ multiple bonds. Due to small size and high electronegativity oxygen exists as diatomic (O_2) molecule. These molecules are held together by weak van der Waals' forces. Hence O_2 is a gas at room temperature.
Sulphur because of its bigger size and lower electronegativity, prefer to form S—S single bonds. Further because of stronger S—S than O—O single bonds, sulphur has a much greater tendency for catenation than oxygen. Thus, sulphur because of its higher tendency for catenation and lower tendency for $p\pi - p\pi$ multiple bonds, forms octa atomic (S_8) molecules, having eight-membered puckered ring structure. Because of bigger size, the force of attraction holding the S_8 molecule together are much stronger. Hence, sulphur is a solid at room temperature.

(iii) All halogens are coloured. It is due to the reason that their molecules absorb light in the visible region as a result of which their electrons get excited to higher energy levels while the remaining light is transmitted. The colour of the halogens is actually the colour of this transmitted light.

30. (a) Write a suitable chemical equation to complete each of the following transformations : [2, 3]

(i) Butan-1-ol to butanoic acid

(ii) 4-Methylacetophenone to benzene-1, 4-dicarboxylic acid

(b) An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

OR

(a) Give chemical tests to distinguish between :

(i) Propanol and propanone

(ii) Benzaldehyde and acetophenone

(b) Arrange the following compounds in an increasing order of their property as indicated :

(i) Acetaldehyde, Acetone, Methyl tert-butyl ketone (reactivity towards HCN)

(ii) Benzoic acid, 3, 4-dinitrobenzoic acid, 4-Methoxy-benzoic acid (acid strength)

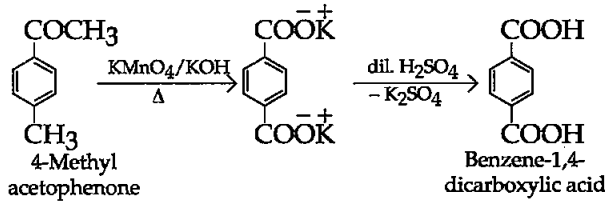
(iii) $CH_3CH_3CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$(acid strength)

Answer : (a) (i)

$$CH_3CH_2CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2CH_2COOH$$

Butan-1-ol — Butanoic acid

(ii)

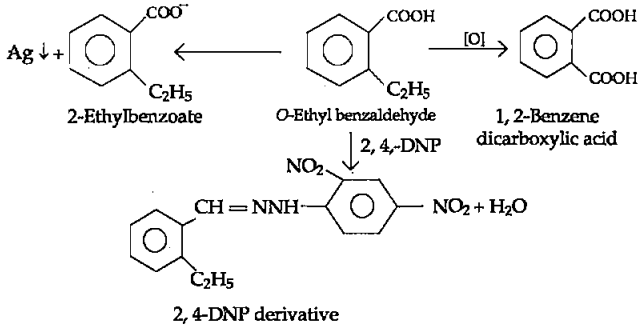


4-Methyl acetophenone — Benzene-1,4-dicarboxylic acid

(b) 1. The given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivatitve and reduces Tollen's reagent It must be an aldehyde.

2. As the compond undergoes cannizzaro reaction, therefore CHO group is directly attached to the benzene ring.

3. On vigrous oxidation, it gives 1, 2-benzene dicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde.



2-Ethylbenzoate — *O*-Ethyl benzaldehyde — 1, 2-Benzene dicarboxylic acid

2, 4-DNP derivative

OR

Answer : (a) (i) Iodoform Test : This test is given by propanone and not by propanol. Propanone on reacting with hot NaOH/I_2 gives a yellow precipitate of CHI_3 while propanol does not.

$$2NaOH + I_2 \rightarrow NaI + NaOI + H_2O$$

$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3 + 3NaOI \rightarrow \underset{\text{yellow ppt.}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COONa} + 2NaOH$$

Sodium hypo-Iodite

(ii) Silver Mirror Test : Benzaldehyde being an aldehyde reduces Tollens' reagent to give silver

mirror test but acetophenone being a ketone does not give this test.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\text{Heat}} \underset{\text{Tollens' reagent}}{}$$

$$C_6H_5COO^- + 2H_2O + 2Ag\downarrow + 4NH_3$$
Silver mirror

(b) (i) Methyl tert - butyl ketone < Acetone < Acetaldehyde.

(ii) 4-methoxybenzoic acid < benzoic acid < 3,4 dinitrobenzoic acid

(iii) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

●●

Chemistry 2012 (Outside Delhi) SET II

Time allowed : 3 hours **Maximum marks : 70**

Note : Except for the following questions, all the remaining questions have been asked in previous set.

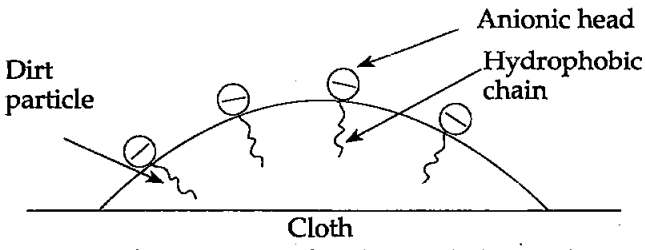
1. **Which stoichiometric defect increases the density of a solid ?**** [1]

2. **What is meant by 'shape selective catalysis' ?** [1]
Answer : Zeolites are shape selective catalysts and shape selective catalysis depends upon the structure of the pores present in the catalyst and size of the reactant and product molecules. ZSM-5 is an example of shape selective catalyst, which is used in converting alcohol directly into gasoline.

3. **What is the role of collectors in Froth Floatation process ?** [1]
Answer : Collectors help in attachment of ore particle to an air bubble in froth *e.g.*, Sodium xanthates.

6. **Write the IUPAC name of Ph – CH = CH – CHO.** [1]
Answer : 3-phenyl prop-2-enal

17. **Explain the cleaning action of soap. Why do soaps not work in hard water ?** [2]
Answer : When soap is rubbed on dirty cloth in water, concentration of soap becomes greater than (CMC) critical micelle concentration, micelle formation takes place. These micelles get adsorb at the dirt or grease



In such a manner that hydrophobic end get adsorbs and anionic head remains at the surface.

Therefore dirt particle become negatively charged and when rinsing is done, this particle moves along with water and clothes become free from dirt or grease.

In soap sodium or potassium salts of fatty acids are present *e.g.*, $C_{17}H_{35}COO^-Na^+$ (sodium stearate) when it is added in hard water, presence of calcium or magnesium salts makes insoluble salts of Ca or Mg with carboxylate ion called scum which stick to cloth as gummy mass.

20. **A voltaic cell is set up at 25°C with the following half cells :**

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)

Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential. [3]

$E_{Ni^{2+}/Ni} = -0.25$ V and $E^\circ_{Al^{3+}/Al} = -1.66$ V. ($\log 8 \times 10^{-6} = -0.54$)

Answer :

$Al \rightarrow Al^{3+} + 3e^-$

$Ni^{2+} + 2e^- \rightarrow Ni$

$2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni$

$E^\circ_{cell} = E^\circ_{red} - E^\circ_{ox}$

$E^\circ cell = (-0.25) - (-1.66)$

$= 1.41$ V

$$E^\circ_{Mn+/M} = E^\circ_{cell} = \frac{0.0591}{6} \log \frac{[Al^{+3}]^2}{[Ni^{+2}]^3}$$

$$E^\circ_{Mn+/M} = 1.41 = \frac{0.0591}{6} \log \frac{(1\times10^{-3})^2}{(5\times10^{-1})^3}$$

$$= 1.41 - 0.00985 \log \frac{1000\times10^{-3}}{125\times10^{-3}}$$

$$= 1.41 - 0.00985 \log 2\times10^{-6}$$

$$= 1.41 - (0.00985 \times -0.54)$$

$$= 1.41 - 0.005319 = 1.415 \text{ V}$$

**** Answer is not given due to change in present syllabus.**

23. Explain the following observations :

(i) Many of the transition elements are known to form interstitial compounds.

(ii) There is a general increase in density from titanium (Z = 22) to copper (Z = 29).

(iii) The members of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series. **[3]**

Answer : (i) Transition elements are known to form interstitial compounds because these elements are capable of entrapping smaller atoms of other elements such as H,C and N in the interstitial sites in their crystal lattice.

(ii) It is due to increase in atomic mass whereas atomic size decreases from Ti to Cu .Therfore, density goes on increasing.

(iii) Because of the comparable energies of 5*f*, 6*d* and 7*s* orbitals in actinoids, they exhibit larger number of oxidation states than the corresponding members of lanthanoid series.

27. Explain the following terms giving a suitable example for each : **[3]**

(i) Elastomers

(ii) Condensation polymers

(iii) Addition polymers.

Answer : (i) Elastomers : Their polymer chain are held together by weakest intermolecular forces so that they can be stretched. That is why they exhibit elastic properties and are rubber-like solids. *eg.*, : Buna–S, Buna–N etc.

(ii) Condensation Polymers : They are formed by repeated condensation reaction between two different bi or tri-functional monomeric units with the elimination of smaller molecules such as water, alcohol, HCl etc. *e.g.*, : Nylon 6, 6.

(iii) Addition Polymers : They are formed by the repeated addition of monomer molecules having double or triple bonds. *eg* : Polyethylene.

30. (a) Draw the structures of the following molecules : **[5]**

(i) H_3PO_2, (ii) ClF_3.**

(b) Explain the following observations :

(i) Nitrogen is much less reactive than phosphorus.**

(ii) Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water.

(iii) Sulphur has a greater tendency for catenation than oxygen in the same group.

OR

(a) Draw the structures of the following molecules :

(i) N_2O_5, ** (ii) $HClO_4$.

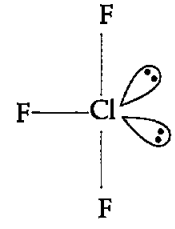
(b) Explain the following observations :

(i) H_2S is more acidic than H_2O.

(ii) Fluorine does not exhibit any positive oxidation state.

(iii) Helium forms no real chemical compound.

(ii)



T shape, ClF_3
sp^3d hybridisation

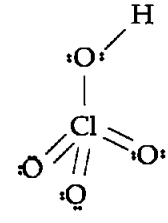
b(i) Due to N≡N triple bond in N_2 molecule, it is inert and hence is less reactive as compared to phosphorous which has P-P single bond,which makes it more reactive.

(ii) In case of HF, average two intermolecular hydrogen bonds are present. As a result, Vander Waals forces of attraction increases in water molecule and hence, boiling point increases.

(iii) Because S–S bond is stronger than O–O bonds as there is more interelectronic repulsion in O–O than in S–S.

OR

(a)(ii)



Perchloric acid
($HClO_4$)

** **Answer is not given due to change in present syllabus.**

(b) (i) Because bond dissociation enthalpy of H–S bond in H_2S is less than that of H–O bond in H_2O.

(ii) Flourine is the most electronegative element in nature and it has no *d*-orbitals and therefore, there is no scope for electron promotion. Hence, it can show only –1 oxidation state in its compounds.

(iii) Because it is an inert gas and has very high ionization enthalpy, therefore no real chemical compound of helium is known.

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Chemistry 2012 (Outside Delhi) SET III

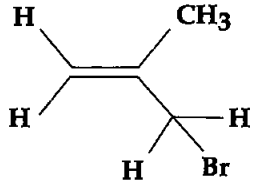
Time allowed : 3 hours **Maximum marks : 70**

Note : Except for the following questions, all the remaining questions have been asked in previous sets.

1. What are *n*-type semiconductors ?** [1]

4. What is the basicity of H_3PO_2 acid and why ? ** [1]

5. Write the IUPAC name of the following : [1]



Answer : 3 Bromo-2-methyl propene.

7. Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain. [1]

Answer :

$$\begin{array}{l}\text{CHO}\\|\\(\text{CHOH})_4\\|\\\text{CH}_2\text{OH}\end{array} + \text{HI} \xrightarrow{\Delta}$$

$$\underset{\text{n–hexane}}{\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3}$$

8. What is the cause of a feeling of depression in human beings ? Name a drug which can be useful in treating this depression. [1]

Answer : The inability to achieve one's goal and extra work may cause the level of noradrenaline low, as a result the signal-sending activity becomes low and the person suffers from depression. Tranquilizers such as Equanil can help in treating depression.

11. Explain the role of each of the following : [2]

(i) NaCN in the extraction of silver.

(ii) SiO_2 in the extraction of copper.

Answer : **(i)** Dil. NaCN solution is used to leach silver (Ag) from silver ore in the presence of air. The silver metal is obtained by replacement.

$$4Ag + 8CN^- + 2H_2O + O_2 \rightarrow 4[Ag(CN)_2]^- + 4OH^-$$

$$2[Ag(CN)_2] + Zn \rightarrow [Zn(CN)_4]^{2} + 2Ag$$

(ii) SiO_2 is used to remove impurity and it reacts with FeO to form easily removable feasible slag

$$FeO + SiO_2 \rightarrow \underset{\text{slag}}{FeSiO_3}$$

22. Write three distinct features of chemisorption which are not found in physisorption. [3]

Answer : The three distinct features of chemisorption are :

(i) It is irreversible.

(ii) It occurs by chemical bond formation and hence requires activation energy.

(iii) It is highly specific in nature.

23. Explain each of the following observations : [3]

(i) With the same *d*-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.

(ii) Actinoids exhibit a much larger number of oxidation states than the lanthanoids.

(iii) There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.

Answer : **(i)** Cr^{2+} is reducing because when it loses one electron to form Cr^{3+}: $[Ar]3d^3$, it has three unpaired electrons in lower energy *d*-orbitals which are more stable whereas M^{3+} is oxidizing because after gaining one electron it becomes Mn^{2+} which has more stable electronic configuration due to half-filled *d*-orbitals Mn^{2+}:$[Ar]3d^5$

(ii) Due to comparable energies of 5*f*, 6*d* and 7*s* orbitals and unpaired electrons in these orbitals, actinoids exhibit much larger number of oxidation states than the lanthanoids.

(iii) Because along transition series, nuclear charge increases which tends to decrease the size but the addition of electrons in the penultimate *d*-subshell increases the screening effect which counter balances the effect of increased nuclear charge. Thus, atomic radii does not change.

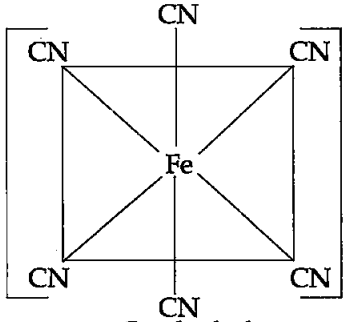
**** Answer is not given due to change in present syllabus.**

24. Name the following coordination entities and describe their structures : [3]

(i) $[Fe(CN)_6]^{4-}$ (ii) $[Cr(NH_3)_4Cl_2]^+$ (iii) $[Ni(CN)_4]^{2-}$

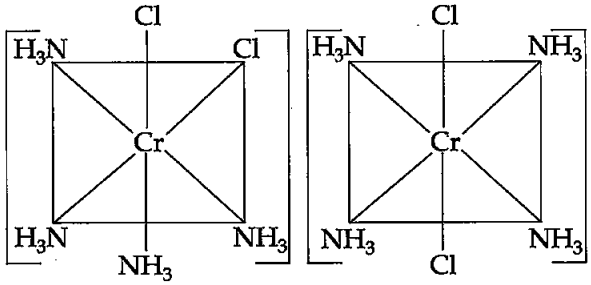
(Atomic Numbers Fe = 26, Cr = 24, Ni = 28)

Answer : (i) $[Fe(CN)_6]^{4-}$: Hexacyanoferrate (II) ion.



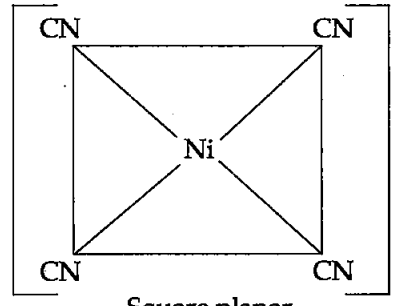
Octahedral

(ii) $[Cr(NH_3)_4Cl_2]^+$: Tetraamminnedichlorido Chromium (III) ion



cis form (Octahedral) trans-form (Octahedral)

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



Square planar

26. Define the following as related to proteins : [3]

(i) Peptide linkage

(ii) Primary structure

(iii) Denaturation.

Answer : (i) Peptide linkage is the amide linkage between two amino acids to form proteins and polypeptides. CO-NH is peptide linkage.

(ii) The simple linear structure of a protein molecule in a specific sequence in which various amino acids are present.

(iii) When a protein in its native form is subjected to any physical change like change in temperature or chemical change like change in pH, the H-bonds gets disturbed. Due to this globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

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Chemistry 2012 (Delhi) SET I

Time allowed : 3 hours **Maximum marks : 70**

1. What is meant by 'doping' in a semiconductor ? [1]**

2. What is the role of graphite in the electrometallurgy of aluminium ? [1]

Answer : Graphite is used as anode and useful for the reduction of Al_2O_3 into Al.

3. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why ? [1]**

4. Give the IUPAC name of the following compound.

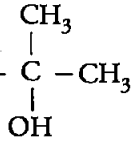
$CH_2 = C - CH_2Br$

CH_3

Answer : 3-bromo-2-methylpropene

5. Draw the structural formula of 2-methyl-propan-2ol molecule. [1]

Answer :



6. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions : ethanol, propanal, propanone, butanone.

Answer : Butanone < Propanone < Proponal < Ethanol

7. Arrange the following in the decreasing order of their basic strength in aqueous solutions :

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3$ N and NH_3 [1]

Answer : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

** Answer is not given due to change in present syllabus.

8. Define the term, 'homopolymerisation' giving an example. [1]

Answer : Polymerisation involving the presence of only one monomer is called homopolymerisation. *e.g.*, polyethene is a homopolymer

$$n(CH_2 = CH_2) \rightarrow \text{-}(CH_2 - CH_2)\text{-}_n$$

Ethene Polyethene

9. A 1.00 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has the boiling point of 100.18 °C. Determine the Van't Hoff factor for trichloroacetic acid. (K_b for water = 0.512 K kg mol^{-1}) [2]

OR

Define the following terms :

(i) Mole fraction (ii) Isotonic solutions

(iii) Van't Hoff factor (iv) Ideal solution

Answer : Given,

$\Delta T_b = 373.18 - 373. = 0.18$ K.

$K_b = 0.512$ K kg mol^{-1}

$m = 1$

$\Delta T_b = i K_b m$

$$i = \frac{\Delta T_b}{K_b m} = \frac{0.18}{0.512 \times 1} = 0.35$$

OR

(i) Ratio of the number of moles of a component in a mixture to the total number of moles in the mixture is called the mole fraction of that component. It is denoted by '*x*'.

(ii) Two solutions having the same molar concentration are said to be isotonic solutions. *e.g.*, All intravenous injections must be isotonic with body fluids.

(iii) The ratio of observed colligative property to the calculated colligative property is called the Van't Hoff factor. It is denoted by '*i*'.

(iv) Solutions that follow Raoult's law at all temperatures and concentrations are called ideal solutions.

0. What do you understand by the 'order of a reaction' ? Identify the reaction order from each of the following units of reaction rate constant : [2]

(i) L^{-1} mol s^{-1}

(ii) L mol^{-1} s^{-1}

Answer : The sum of the powers to which the concentration of reactants are raised in the rate law expression is called the order of a reaction.

(i) Zero order reaction

(ii) Second order reaction.

11. Name the two groups into which phenomenon of catalysis can be divided. Give an example of each group with the chemical equation involved. [2]

Answer : Catalysis can be positive, that is, it increases the rate of the reaction or negative *i.e.*, decreases the rate of reaction. Depending on the phase of the reactants and the catalyst, catalysis can be :

(i) Homogenous Catalysis : The reactants and catalyst are in the same phase.

e.g., $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(ii) Heterogeneous catalysis : The reactants and catalyst are in different phase.

$4NH_3(g) + 5SO_2(g) \xrightarrow{Pt(s)} 4NO + 5S + 6H_2O$

12. What is meant by coagulation of a colloidal solution ? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out. [2]

Answer : The process of setting of colloidal particles is called coagulation of sol. Methods of coagulation are :

(i) Electrophoresis : In this process, the colloidal particles move towards opposite charged electrodes and get discharged and precipitated.

(ii) Mixing two Oppositely Charged Sols : Equal proportions of oppositely charged sols are mixed, they get neutralized and get precipitated.

(iii) Dialysis : Electrolytes are removed from the sol and colloid becomes unstable and gets coagulated.

13. Describe the principle involved in each of the following processes. [2]

(i) Mond process for refining of Nickel.

(ii) Column chromatography for purification of rare elements.

Answer : **(i)** Nickel combined with carbon monoxide to form volatile complex which is further decomposed to get back pure nickel.

$$Ni(g) + 4CO(g) \xrightarrow{330\text{-}350K} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4(g)}$$

$$Ni(CO)_4(g) \xrightarrow[450\text{–}470K]{\Delta} \underset{\text{Nickel}}{Ni} + 4CO$$

(ii) The basic principle involved in column chromatography is that different elements present in a mixture are adsorbed on adsorbent at different extents.

14. Explain the following giving an appropriate reason in each case. [2]

(i) O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so.

(ii) Structures of xenon fluorides cannot be explained by Valence Bond approach.

Answer : (i) Due to the difference in atomic size of oxygen and fluorine and the property of oxygen to form multiple bonds with metals, O_2 exceeds F_2, stabilize higher oxidation states.

(ii) For explaining the structures of xenon fluorides, we need to use VSEPR and hybridization theories because in VBT, covalent bonds are formed by overlapping of half filled atomic orbital. But xenon has fully filled electronic configuration.

15. Complete the following chemical equations : [2]

(i) $Cr_2O_7^{2-} + H^+ + I^-$

(ii) $MnO_4^- + NO_2^- + H^+ \rightarrow$

Answer :

(i) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

(ii) $2MnO_4^- + 5NO_2^- + 6H^+ \rightarrow 2Mn^{2+} + 3H_2O + 5O_3^-$

16. What is meant by (i) peptide linkage (ii) biocatalysts ? [2]

Answer : (i) Peptides linkage is the amide bond that helps to connect amino acids to form proteins. It is formed between –COOH and $–NH_2$ group of two amino acids with the loss of water molecule.

(ii) Biocatalysts are enzymes that catalyses the biochemical reactions in the bodies of living organisms. *e.g.*, Amylase.

17. Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule. [2]

Answer : Two reactions which can't be explained by open chain structure of glucose are :

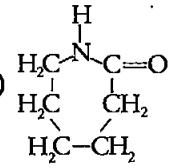
(i) Despite having the aldehyde group, glucose does not gives 2, 4 –DNP test.

(ii) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free –CHO group.

18. Draw the structure of the monomer for each of the following polymers : [2]

(i) Nylon 6, (ii) Polypropene.

Answer :

(i) 
Caprolactum

(ii) $CH_3—CH=CH_2$
Propene

19. Tungsten crystallizes in body centered cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of tungsten atom ? [3]**

OR

Iron has a body centered cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number. (At mass of Fe = 55.845 u)**

20. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2K. (K_f for water = 1.86 K kg mol^{-1}) [3]

Answer : Given,

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$i = 2, \Delta T_f = 2K$$

$$M = 74.5$$

$$\Delta T_f = iMK_f$$

$$2 = 2 \times 1.86, \frac{\text{Mass of KCl}}{74.5}$$

$$\text{Mass of KCl} = \frac{74.5}{1.86} = 40.05 \text{ gm}$$

21. For the reaction [3]

$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$

the following data were collected. All the measurements were taken at 263 K :

Experiment No.	Initial [NO] (M)	Initial $[C_2]$ (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

****Answer is not given due to change in present syllabus.**

(c) What is the initial rate of disappearance of Cl_2 in exp. 4 ?

Answer : (a) Rate law $k = k[NO]^2[Cl_2]^1$

(b) $R = k[NO]^2[Cl_2]^1$

$$k = \frac{R}{[NO]^2} = \frac{0.60}{(0.15)^2(0.15)^1}$$

$$= \frac{0.60}{(0.15)^3} = 177.75 \text{ mol}^{-2}\text{L}^2 \text{ min}^{-1}$$

(c) $R_4 = k[NO]^2[Cl_2]^1$

$= 177.75 \times (0.25)^2 (0.25)$

$= 2.78$ M/min.

22. How would you account for the following ? [3]

(i) Many of the transition elements are known to form interstitial compounds.

(ii) The metallic radii of the third (5*d*) series of transition metals are virtually the same as those of the corresponding group members of the second (4*d*) series.

(iii) Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.

Answer : (i) Transition metal lattice have voids and hence these voids can trap small atoms like H, C and N to form interstitial compounds.

(ii) It is because electrons first fill the 4*f* orbitals and than the 5*d*-orbitals causing decline in radii of third (5*d*) series.

(iii) This is because of the comparable energies of 5*f*, 6*d* and 7*s* orbitals so all of them can participate

23. Give the formula of each of the following coordinat... ntities : [3]

(i) Co^{3+} ion is bound to one Cl^-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.

(ii) Ni^{2+} ion is bound to two water molecules and two oxalate ions.

Write the name and magnetic behavior of each of the above coordination entities.

(At. Nos. Co = 27, Ni = 28)

Answer : (i) $[Co(NH_3)(en)_2Cl]^{2+}$ Amminebis (ethylenediamine) chlorido cobalt (III) ion, diamagnetic.

(ii) $[Ni(H_2O)_2 (C_2O_4)_2]^{2-}$

Diaquadioxalatonickelate (II) ion, paramagnetic.

24. Although chlorine is an electron withdrawing group, yet it is ortho, para-directing in electrophilic aromatic substitution reactions. Explain why it is so ? [3]

Answer : Due to resonance, electron density is increased on ortho and para positions for electron donating (via resonance) groups like chlorine. Thus chlorine is an electron withdrawing group yet it electrophilic is ortho, para-direction in aromatic substitution reaction.

25. Draw the structure and name the product formed if the following alcohols are oxidized. Assume that an excess of oxidizing agent is used. [3]

(i) $CH_3CH_2CH_2CHt_2OH$, (ii) 2-butanol

(iii) 2-methyl-l-propanol

Answer : (i)

$$\underset{\text{Butan-1-ol.}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow[CrO_3-H_2SO_4]{[O]} \underset{\text{Butanoic acid}}{CH_3-CH_2-CH_2-COOH}$$

(ii)

$$\underset{\text{But-2-enol}}{CH_3-CH=CH_2-CH_2-OH} \xrightarrow[PCC]{[O]} \underset{\text{Butanoic acid}}{CH_3-CH=CH-CHO}$$

(iii)

$$\underset{\text{2-methyl propan-1-ol}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH} \xrightarrow{[O]} \underset{\text{2-MethylPropanoic acid}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH-COOH}$$

26. Write chemical equations for the following conversions : [3]

(i) Nitrobenzene to benzoic acid.

(ii) Benzyl chloride to 2-phenylethanamine.

(iii) Aniline to benzyl alcohol.

Answer : (i)

$$\underset{\text{(Nitrobenzene)}}{(C_6H_5NO_2} \xrightarrow[BaSO_4]{H_2/Pd} \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[HCl]{NaNO_2} \underset{\text{Benzenediazonium chloride}}{C_6H_5\overset{+}{N}_2Cl^-)} \downarrow CuCN$$

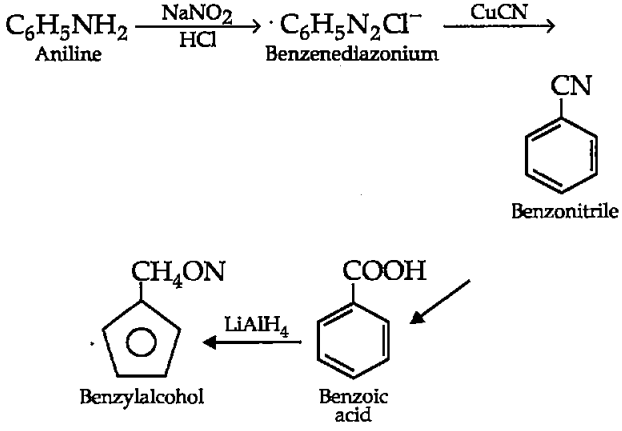
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xleftarrow[H^+]{H_2O} \underset{\text{Benzonitrile}}{C_6H_5-CN}$$

(ii)

$$\underset{\text{Benzylcholride}}{C_6H_5-CH_2Cl} + KCN \longrightarrow \underset{\text{Phenylethanenitrile}}{C_6H_5-CH_2-CN}$$

$$\xrightarrow{LiAlH_4 \downarrow} \underset{\text{2-phenylethana mine}}{C_6H_5CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH_2}}}$$

(iii)



27. What are the following substances ? Give one example of each one of them. [3]

(i) Tranquilizers

(ii) Food preservatives

(iii) Synthetic detergents.

Answer : (i) Tranquilizers are drugs that act on the central nervous system to get relief from anxiety, stress etc. They are used in treatment of stress related mental disorders *eg.*,Equanil.

(ii) These are chemicals used to preserve food by protecting it against microbial growth. *e.g.*, Sodium benzoate.

(iii) Synthetic detergents have all the properties of soap but they do not precipitate in hard water. *e.g.*, Sodium *p*-dodecyl benzenesulphonate.

28. (a) What type of a battery is the lead storage battery ? Write the anode and the cathode reactions and the overall reactions occurring in a lead storage battery when current is drawn from it. [2],[3]

(b) In the button cell, widely used in watches, the following reaction takes place.

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow$$

$$Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$$

Determine E° and ΔG° for the reaction

(Given : $E^\circ_{Ag^+/Ag} = +0.80V, E^\circ_{Zn^{2+}/Zn} = -0.76$ V)

OR

(a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1} ?

Answer : (a) Lead storage battery is secondary cell and can be recharged by passing current through it.

At anode : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$

At cathode : $PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+ + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O$

Overall cell reaction :

$$Pb + PbO_2 + H_2SO_4\,(aq) \rightarrow 2PbSO_4 + 2H_2O$$

(b) $E^\circ cell = 0.8 - (-0.76) = 1.56$ V

$\Delta G^\circ = -nFE^\circ_{Cell}$

$= -2 \times 96500 \times 1.56$

$= -301$ kJ mol^{-1}

OR

(a) Molar conductivity of a solution is the conductance of the solution with one mole of electrolyte placed between electrodes 1 cm apart. With dilution, molar conductivity of weak electrolytes increases sharply and for strong electrolytes also, it increases.

(b) $k = 0.146 \times 10^{-3}$ cm$^{-1}\Omega^{-1}$

$R = 1500\Omega$

$$\text{Specific conductance} = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$\text{Cell constant} = \kappa R = 0.146 \times 10^{-3} \times 1500$$

$$= 0.219 \text{ cm}^{-1}$$

29. (a) Complete the following chemical reactions. equations : [2],[3]

(i) $P_4 + SO_2Cl_2 \rightarrow$**

(ii) $XeF_6 + H_2O \rightarrow$

(b) Predict the shape and asked the angle (90° or more or less) in each of the following cases :

(i) SO_3^{2-} **and the angle O–S–O**

(ii) ClF_3 **and the angle F–Cl–F**

(iii) XeF_2 **and the angle F–Xe–F**

OR

(a) Complete the following chemical equations:

(i) $NaOH + Cl_2 \rightarrow$

(hot and conc.)

(ii) $XeF_4 + O_2F_2 \rightarrow$

(b) Draw the structures of the following molecules :

(i) H_3PO_2**

(ii) $H_2S_2O_7$

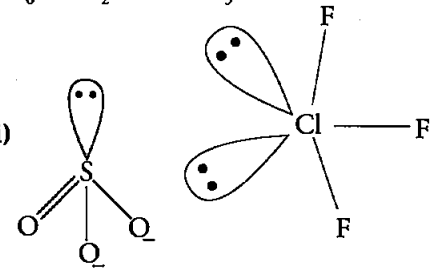
(iii) $XeOF_4$

** Answer is not given due to change in present syllabus.

Answer :

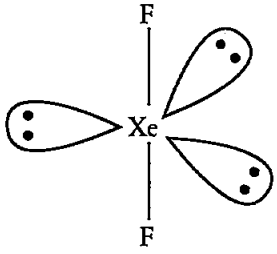
(ii) $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

(b) (i)



SO_3^{2-} more than 90°

ClF_3 less than 90°



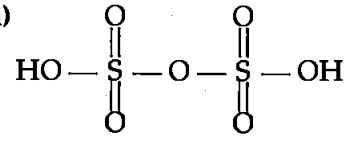
XeF_2 more than 90^0

OR

(a)(i) $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

(ii) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

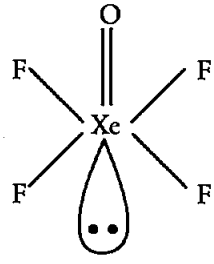
(ii)



Disulphuric acid

$H_2S_2O_7$

(iii)



$XeOF_4$

30. (a) Illustrate the following name reactions giving suitable example in each case : [2],[3]

(i) Clemmensen reduction

(ii) Hell-Volhard-Zelinsky reaction

(b) How are the following conversions carried out ?

(i) Ethylcyanide to ethanoic acid

(ii) Butan-l-ol to butanoic acid

(iii) Benzoic acid to *m*-bromobenzoic acid

OR

(a) Illustrate the following reactions giving a suitable example for each :

(i) Cross aldol condensation, (ii) Decarboxylation

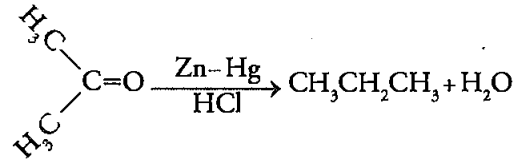
(b) Give simple tests to distinguish between the following pairs of compounds :

(i) Pentan-2-one and Pentan-3-one

(ii) Benzaldehyde and Acetophenone

(iii) Phenol and Benzoic acid

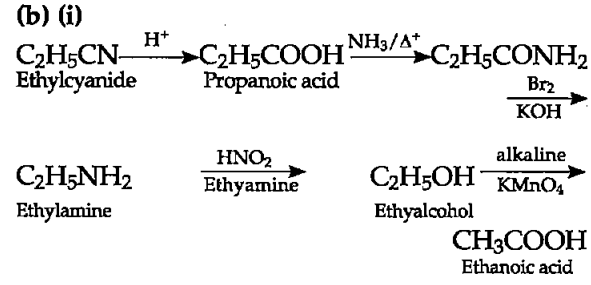
Answer : (a) (i) Aldehydes and ketones are reduced to CH_2 group on treatment with zinc-amalgam and conc. HCl.



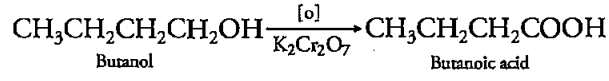
(ii) Carboxylic acids containing α-hydrogen atom gives halo carboxylic acids on treatment with halogens in the presence of red phosphorous.

$$CH_3COOH + Cl_2 \xrightarrow{\text{Red P}} ClCH_2COOH + HCl$$

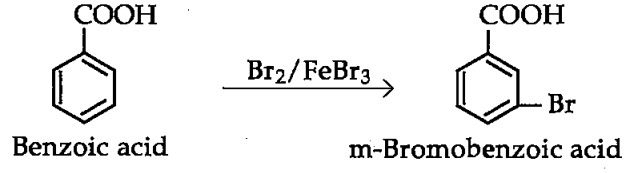
(b) (i)



(ii)

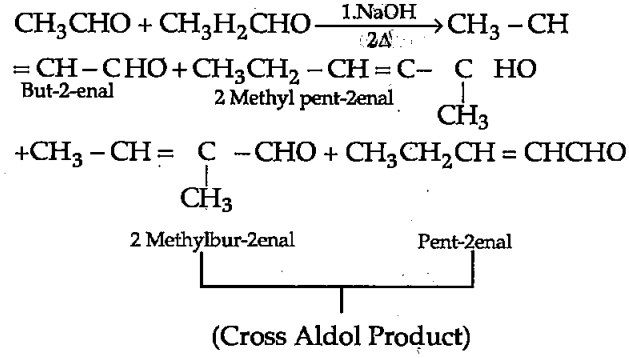


(iii)



OR

(a) (i) When aldol condensation is carried out between two different aldehydes or ketones it is called cross aldol condensation.



(ii) Carboxylic acid lose carbon dioxide to form hydrocarbon, when their salts are heated with sodium. The reaction is known as decarboxylation reaction

$$R-COONa \xrightarrow[Heat]{NaOH\&CaO} R-H + Na_2CO_3$$

(b)(i) Pentan-2-one gives iodoform test but pentan-3-one does not.

$$\underset{\text{Pentan-2-one}}{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3} + 3NaOI \rightarrow CH_3CH_2CH_2COONa + \underset{\substack{\text{Iodoform}\\\text{(yellow ppt)}}}{CHI_3\downarrow} + 2NaOH$$

$$\underset{\text{Pentan-3-one}}{CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3} + NaOI \rightarrow \text{No yellow ppt. of Iodoform.}$$

(ii) Benzaldehyde does not gives iodoform test but Acetophenone gives iodoform test.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \rightarrow \underset{\substack{\text{Iodoform}\\\text{(yellow ppt.)}}}{CHI_3\downarrow} + C_6H_5COONa + 2NaOH$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + NaOI \rightarrow \text{No yellow ppt. of Iodoform}$$

(iii) Phenol gives violet colour with neutral $FeCl_3$ solution but benzoic acid does not.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \rightarrow \underset{\text{Violet colour}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

$$3C_6H_5COOH + FeCl_3 \rightarrow \underset{\text{Buff Colour}}{(C_6H_5COO)_3Fe} + 3HCl$$

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Chemistry 2012 (Delhi) SET II

Time allowed : 3 hours **Maximum marks : 70**

Note : Except for the following questions, all the remaining questions have been asked in previous set.

1. Write a point of distinction between a metallic solid and an ionic solid other than metallic luster.** [1]

11. Describe a conspicuous change observed when : [2]

(i) a solution of NaCl is added to a sol of hydrated ferric oxide.

(ii) a beam of light is passed through a solution of NaCl and then through a sol.

Answer : (i) Coagulation of ferric hydroxide sol. would take place.

(ii) NaCl solution is transparent so when beam of light is passed, no tyndall effect is produced. But on passing through solution the path of light becomes visible due to Tyndall effect.

13. Describe the following : [2]

(i) The role of cryolite in electro-metallurgy of aluminium.

(ii) The role of carbon monoxide in the refining of crude nickel.

Answer : (i) Cryolite lowers the melting point of the mixture and brings conductivity. Therefore, it is mixed with alumina during metallurgy of aluminium.

(ii) Carbon monoxide forms a volatile complex with nickel. The volatile complex is then subjected to high temperature to get pure metal through decomposition.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{300-350K} \underset{\text{(Nickel tetracarbonyl)}}{Ni(CO)_4}$$

$$Ni(CO_4) \xrightarrow{400-450K} \underset{\text{Pure}}{Ni} + 4CO$$

14. What is meant by (i) peptide linkage, (ii) biocatalysts ? [2]

Answer : (i) Peptide Linkage : It is the linkage between amino acids, formed due to loss of a water molecule and amide linkage is formed.

$$\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}$$

(ii) Biocatalysts : Biocatalysts are enzymes which are used to perform chemical reactions on organic compounds.

18. Write the main structural difference between DNA and RNA. Of the two bases, thymine and uracil, which one is present in DNA ? [2]

Answer :

	DNA	RNA
1.	DNA has deoxyribose sugar.	1. RNA has ribose sugar.
2.	It has double helical structure.	2. It is single strand-ed.
3.	It is less reactive due to presence of C-H bonds.	3. It has larger grooves so it is more reactive.

DNA contains thymine base and uracil base is present in RNA.

**** Answer is not given due to change in present syllabus.**

23. How would you account for the following ? [3]

(i) With the same d-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidizing agent.

(ii) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.

(iii) Most of the transition metal ions exhibit characteristic in colours in aqueous solutions.

Answer : (i) Cr^{2+} has d^4 configuration. It gets oxidized to Cr^{3+} with electronic configuration d^3 which is more stable. Therefore, Cr^{2+} is a reducing agent. Mn^{3+} has d^4 configuration. It gets reduced to Mn^{+2} with d^5 configuration. This is half-filled d-orbital and is stable. Therefore Mn^{3+} is an oxidizing agent.

(ii) Because 5*f*, 6*d* and 7*s* energy levels has small energy gap in the actinoid series. Due to these orbitals actinoids exhibit large number of oxidation states.

(iii) Due to partial absorption of visible light the electron from one orbital gets promoted to another orbital of the *d* subshell. Due to the presence of unpaired electrons transition metals are coloured.

30. (a) Give a possible explanation for each one of the following: [2],[3]

(i) There are two $-NH_2$ groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones.

(ii) Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethylcyclohexanone does not.

(b) An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4, –DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives 1, 2-benzene-di-carboxylic acid. Identify the compound.

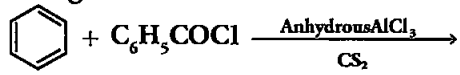
OR

(a) Give chemical tests to distinguish between

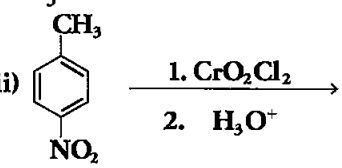
(i) Phenol and Benzoic acid

(ii) Acetophenone and Benzophenone

(b) Write the structures of the main products of following reactions :

(i) 

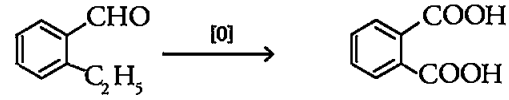
(ii) $H_3C-C\equiv C-H \xrightarrow{Hg^{2+},H_2SO_4}$

(iii) 

Answer : (a) (i) Semicarbazide show resonance involving one of the two $-NH_2$ groups, which is attached to the carboxyl carbon atom. Due to which electron density on $-NH_2$ group involved in resonance decreases. So it cannot act as nucleophile. Other $-NH_2$ group can act as nucleophile to produce semicarbazones with aldehydes and ketones.

(ii) In cyclohexanone CN^- can easily attack without any steric hindrance. But in 2, 4, 6 – Trimethylcyclohexanone due to presence of methyl groups steric hindrance is produced and CN^- cannot attack effectively.

(iii) $C_9H_{10}O$ is aldehyde because it reduces Tollen's reagent. It undergoes Cannizaro's reaction therefore it is substituted benzaldehyde. It gives 1, 2, Benezene-di carboxylic acid. The compound is 2-Ethylbenzaldehyde.



2Ethylbenzaldehyde 1,2-Benzene-dicarboxylic acid

OR

(a)(i) Phenol gives violet colour with neutral $FeCl_3$ solution but benzoic acid does not.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \rightarrow \underset{\text{Violet colour}}{[Fe(OC_6H_5)]^{3-}} + 3H^+ + HCl$$

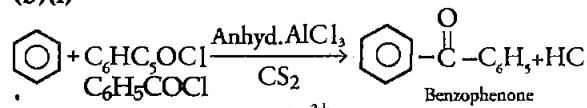
$$\underset{\text{Benzoic acid}}{3C_6H_5COOH} + FeCl_3 \rightarrow \underset{\text{Buff Colour}}{(C_6H_5COO)_3Fe} + 3HCl$$

(ii) Acetophenone gives iodoform test but benzophenone does not

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \xrightarrow{\Delta} C_6H_5COONa + \underset{\substack{\text{Iodoform}\\\text{(yellow ppt)}}}{CHI_3} + 2NaOI$$

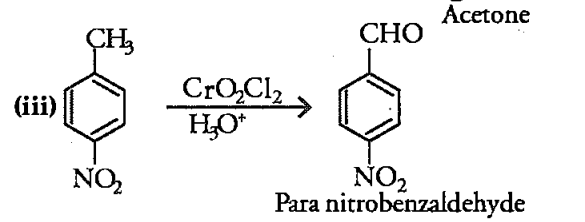
$$\underset{\text{Benzophenone}}{C_6H_5COC_6H_5} \xrightarrow{NaOI} \text{No yellow ppt of Iodoform}$$

(b)(i)



(ii) $CH_3-C\equiv C-H \xrightarrow[H_2SO_4]{Hg^{2+}} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ Acetone

(iii)



Para nitrobenzaldehyde

●●

Chemistry 2012 (Delhi) SET III

Time allowed : 3 hours **Maximum marks : 70**

Note : Except for the following questions, all the remaining questions have been asked in previous sets.

3. Out of PH_3 and H_2S, which is more acidic and why ? [1]

Answer : H_2S is more acidic than PH_3 due to smaller size and higher electronegativity of sulphur. Therefore S-H bond is polar than P-H bond and easy to remove.

5. Draw the structure of hex-1-en-3-ol compound. [1]

Answer :

$$CH_3CH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}H-CH=CH_2$$

12. Explain the following terms giving one example for each : [2]

(i) Micelles

(ii) Aerosol.

Answer : (i) Micelles are aggregates which exhibit colloidal behaviour at higher concentration, with the hydrophilic part outside and the hydrophobic part towards the oil and dirt particle. *e.g.*, soap.

(ii) An aerosol is a colloid of fine solid particle or liquid drops in air or another gas. It can be natural or artificial. e.g. dust particle and smoke.

20. 15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at –0.34 °C. What is the molar mass of this material ? (K_f for water = 1.86 K kg mol^{-1}) [3]

Answer : Given,

$W_1 = 15$ g, $W_2 = 450$ g

$K_f = 1.86$ K kg/mol

$\Delta T_f = -0.34°C$

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{W_1 \times M_2}$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{W_1 \times \Delta T_f} = \frac{1.86 \times 15 \times 1000}{450 \times 0.34}$$

$M_2 = 182.35$ g / mol

22. Explain the following observations giving an appropriate reason for each : [3]

(i) The enthalpies of atomization of transition elements are quite high.

(ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition metals (*i.e.*, 3rd series).

(iii) Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.

Answer : (i) Due to the presence of metallic bonds as a result of large number of valence electrons.

(ii) The presence of valence electrons and unpaired *d*-orbital electrons help heavy transition metals to form metallic bonds.

(iii) Due to stability of Mn^{2+} because of half filled-subshell ($3d^5$) it does not gets oxidized. But Fe^{2+} has $3d^6$ configuration and it can lose one electron to become $3d^5$ which is stable. Therefore it is easily oxidized.

23. Write the name, the structure and the magnetic behavior of each of the following complexes : [3]

(i) $(Pt(NH_3)Cl(NO_2)]$, (ii) $(Co(NH_3)_4Cl_2]Cl$

(iii) $Ni(CO)_4$

(At. Nos. Co = 27, Ni = 28, Pt = 78)

Answer : (i) Amminechloridonitrito–N-platinum **(ii)**, trigonal planar, diamagnetic.

(II) Tetra-ammine dichlorido cobalt **(III)** chloride, octahedral, diamagnetic

(iii) Tetracarbonyl nickel (0), Tetrahedral, diamagnetic

27. Explain the following terms giving one example of each type: [3]

(i) Antacids,

(ii) Disinfectants,

(iii) Enzymes.

Answer : (i) Substances consumed to reduce acidity in the stomach by neutralizing excess HCl produced by the stomach. *e.g.* Milk of magnesia.

(ii) Disinfectants are chemicals used to kill microorganism, applied only to non-living objects like floors and drains. *e.g.* 1% phenol solution.

(iii) Enzymes are structurally globular proteins that catalyse biochemical reactions in living organisms *e.g.* Trypsin.

30. Draw the molecular structures of following compounds : [2],[3]

(i) XeF_6 (ii) $H_2S_2O_8$

(b) Explain the following observations :

(i) The molecules NH_3 and NF_3 have dipole moments which are of opposite direction.**

(ii) All the bonds of PCl_5 molecule are not equivalent.**

(iii) Sulphur in vapour state exhibits paramagnetism.

OR

(a) Complete the following chemical equations:

(i) $XeF_4 + SbF_5 \rightarrow$ (ii) $Cl_2 + F_2$ (excess) $\rightarrow$

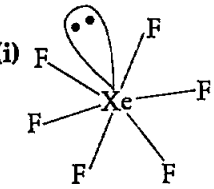
(b) Explain each of the following :**

(i) Nitrogen is much less reactive than phosphorus.

(ii) The stability of +5 oxidation state decreases down group 15.

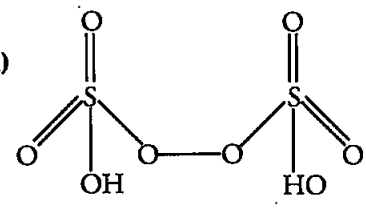
(iii) The bond angles (O-N-O) are not of the same value in NO_2^- and NO_2^+.

Answer : (a) (i)



XeF_6

(ii)



$(H_2S_2O_8)$

(b) (i) Fluorine is more electronegative than nitrogen while hydrogen is less electronegative than nitrogen resulting in opposite dipole moments of NH_3 and NF_3. Dipole points towards N in NH_3 and towards F in NF_3.

OR

(a) (i) $XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$

(ii) $Cl_2 + \underset{\text{(excess)}}{3F_2} \rightarrow 2ClF_3$

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