

## ISM M.Sc. Chemistry Entrance-2009

Each question is of 10 marks. **Parts of a single question** must be answered continuously at one place.

1.
  - (a) Relate ionization potentials of the elements with the degree of penetration of s, p, d and f orbitals of the same quantum number.
  - (b) Explain the problems of metal extraction from sulfide ores by direct reduction with carbon or hydrogen.
  - (c) Indicate the position of the lone pairs of electrons in  $\text{ClF}_3$  molecule and indicate the most stable structure of the molecule in the light of VSEPR theory.
  - (d) A colourless aqueous solution of a metal salt gives white precipitate with  $\text{NH}_4\text{OH}$  and also with  $\text{NaOH}$ . In both the cases the precipitate becomes soluble in both the precipitating agents. Identify the metal ion.
  - (e) Explain the increase in acid strength of the boric acid in the presence of glycerol in an aqueous solution.
  
2.
  - (a) An alkane of mol. wt. 84 gives one monochloro derivative. Write the structure of the alkane.
  - (b) How can you convert cyclohexene to hex-1, 6-diol?
  - (c) What is the reagent that selectively reduces one nitro group of m-dinitro benzene?
  - (d) Methyl-mesitoate does not undergo hydrolysis with dilute acid but why it readily hydrolyses with conc.  $\text{H}_2\text{SO}_4$ ?
  - (e) p-hydroxy toluene (p-cresol) on Reimer-Tiemann reaction produces two products. Give the mechanism of formation of the two products?
  
3.
  - (a) The total hydration energies of  $\text{LiI}$  and  $\text{KI}$  are  $-824$  and  $-627$  kJ/mol and the corresponding lattice energies are  $-763$  and  $647$  kJ/mol respectively. Compare the solubility of the two salts in water.
  - (b) Indicate the charges on  $\text{AgCl}$  colloid prepared from (i) dilute  $\text{NaCl}$  and slight excess of dilute  $\text{AgNO}_3$  solution and (ii) dilute  $\text{AgNO}_3$  and slight excess of dilute  $\text{NaCl}$  solution.
  - (c) Accurately 100gm water contains 1 gm urea and 2gm sucrose at 298 K. The vapor pressure of water at 298 K is 23.756 torr. Calculate the vapor pressure of the solution.
  - (d)  $E^0_{\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}} = 0.36\text{V}$  and  $E^0_{\text{Fe}(\text{aq})^{3+}/\text{Fe}(\text{aq})^{2+}} = 0.771\text{V}$   
 These values suggest lower stability for  $\text{Fe}(\text{CN})_6^{4-}$  towards oxidation compared to that of aquated  $\text{Fe}^{2+}$ . But practically the phenomenon is reverse. Comment on this observation. (assume all components are at unit activity).
  - (e) Draw the concentration vs. time curve for a consecutive reaction,  $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ .
  
4.
  - (a) Indicate the hybridization schemes for  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{FeF}_6]$  complexes. Estimate the  $\mu_{s.o.}$  for the two complexes  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{FeF}_6]$ . Show the electron distribution for both the complexes following the CF splitting pattern of the 3d orbitals for the two complexes of iron. Calculate the spectroscopic ground term symbol for  $3d^5$  ion.
  - (b) Calculate the pH of  $5.0 \times 10^{-8}$  M  $\text{HCl}$  solution.
  
5.
  - (a) How many structural isomers can be obtained by the replacement of one hydrogen atom of propene with one chlorine atom?
  - (b) Write the reaction steps for the conversion of o-xylene to anthranilic acid.
  
6.
  - (a) Considering reversible carnot cycle of an ideal gas with constant  $C_p$  and  $C_v$  draw the curves (i) S vs. V (ii) H vs. P (iii) T vs. S and (iv) H vs. T (The terms S, V, H, P, T have their usual meanings).
  - (b) Find the pH of a buffer solution containing 0.1 M solution of both  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ . Calculate the change in pH (a) on adding 0.01 mole of  $\text{HCl}$  to 1 litre of the solution and (b) on adding 0.01 mole of  $\text{NaOH}$  to one litre of the solution.

7. (a) Chemical analysis of a sample of uranium mineral shows the presence of 7.89 per cent of  $^{238}\text{U}_{92}$  and  $2.63 \times 10^{-6}$  per cent  $^{226}\text{Ra}_{88}$ . Calculate the decay constant of  $^{238}\text{U}_{92}$ . Half life period of  $^{226}\text{Ra}_{88}$  is 1590 years.
- (b) Draw the plots for the change in compression factor (z) with variable pressure, P for a (i) perfect gas and (ii) real gas at higher temperature, Boyle temperature and lower temperature.
8. (a) The reaction between iodine and acetone
- $$\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$$
- is zero order with respect to iodine. Explain the phenomenon.
- (b) Compare diagrammatically the magnitude of work involved in reversible isothermal and adiabatic expansions when (i) final volumes are same and (ii) final pressures are same for an ideal gas.
9. Write down the structure of ethylene diaminetetracetic acid (EDTA). Indicate the donor points of the EDTA molecule which binds to  $\text{Mg}(\text{II})$  ions in an aqueous solution at a pH  $\sim 10$ . Draw the structure of the  $\text{Mg}(\text{II})$ -EDTA complex showing the chelation. How many chelate rings are produced when  $\text{Mg}(\text{II})$ -EDTA complex is formed ?
10. 2, 4, 6-trinitro-N, N-dimethylaniline is  $40 \times 10^3$  times stronger base than 2, 4, 6-trinitroaniline. Whereas, N, N-dimethylaniline and aniline differ very little in their basic strength. Explain the phenomenon.

Propylene under Markonikov addition with HBr gives isopropyl bromide and under anti-Markonikov addition gives n-propylbromide. Show the mechanism behind these observations.