

# CHEMISTRY

## PAPER – 1

### (THEORY)

(Three Hours)

(Candidates are allowed additional 15 minutes for **only** reading the paper.  
They must NOT start writing during this time.)

*Answer all questions in Part I and six questions from Part II, choosing two questions from Section A, two from Section B and two from Section C.*

*All working, including rough work, should be done on the same sheet as, and adjacent to, the rest of the answer.*

*The intended marks for questions or parts of questions are given in brackets [ ].*

*Balanced equations must be given wherever possible and diagrams where they are helpful.*

*When solving numerical problems, all essential working must be shown.*

*In working out problems use the following data:*

*Gas constant  $R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$*

*$1 \text{ l atm} = 1 \text{ dm}^3 \text{ atm} = 101.3 \text{ J}$ .  $1 \text{ Faraday} = 96500 \text{ Coulombs}$ .*

*Avogadro's number =  $6.023 \times 10^{23}$ .*

### PART I (20 Marks)

*Answer all questions.*

#### Question 1

- (a) Fill in the blanks by choosing the appropriate word/words from those given in the brackets: [5]

(increases, decreases, positive, efficient, 68, non-efficient, no  $\alpha$ -hydrogen,  $\alpha$ -hydrogen, negative, Rosenmund's, greater, Cannizzaro, 74, common-ion effect, lesser, buffer action, diamagnetic, paramagnetic)

- (i) The more \_\_\_\_\_ the standard reduction potential of a metal, the \_\_\_\_\_ is its ability to displace hydrogen from acids.
- (ii) Both ccp and hcp are \_\_\_\_\_ packings and occupy about \_\_\_\_\_ % of the available space.
- (iii) Solubility of silver chloride \_\_\_\_\_ in the presence of sodium chloride because of \_\_\_\_\_.
- (iv) Benzaldehyde undergoes \_\_\_\_\_ reaction on treatment with concentrated sodium hydroxide because it has \_\_\_\_\_ atom.
- (v) The transition metals show \_\_\_\_\_ character because of the presence of unpaired electrons and  $\text{Cu}^+$  is \_\_\_\_\_ because its electronic configuration is  $[\text{Ar}]3d^{10}$ .

This Paper consists of 7 printed pages and 1 blank page.

Turn over

(b) Complete the following statements by selecting the **correct alternative from the [5] choices** given:

(i) The molal freezing point constant of water is  $1.86 \text{ K kg mol}^{-1}$ . Therefore, the freezing point of  $0.1 \text{ M NaCl}$  solution in water is expected to be:

- (1)  $-1.86^\circ\text{C}$
- (2)  $-0.372^\circ\text{C}$
- (3)  $-0.186^\circ\text{C}$
- (4)  $+0.372^\circ\text{C}$

(ii) For a first order reaction the rate constant for decomposition of  $\text{N}_2\text{O}_5$  is  $6 \times 10^{-4} \text{ sec}^{-1}$ . The half-life period for the decomposition in seconds is:

- (1) 11.55
- (2) 115.5
- (3) 1155
- (4) 1.155

(iii) When acetaldehyde is treated with Grignard reagent, followed by hydrolysis the product formed is:

- (1) Primary alcohol
- (2) Secondary alcohol
- (3) Carboxylic acid
- (4) Tertiary alcohol

(iv) The geometry of  $\text{XeF}_6$  molecule and the hybridization of Xe atom in the molecule is:

- (1) Distorted octahedral and  $\text{sp}^3\text{d}^3$
- (2) Square planar and  $\text{sp}^3\text{d}^2$
- (3) Pyramidal and  $\text{sp}^3$
- (4) Octahedral and  $\text{sp}^3\text{d}^3$

(v) In the complexes  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Pt}(\text{en})(\text{H}_2\text{O})_2(\text{NO}_2)(\text{Cl})]^{2+}$  the respective oxidation numbers of central metal atoms are :

- (1) +3 and +4
- (2) +6 and +4
- (3) +6 and +3
- (4) +3 and +3

(c) Answer the following questions: [5]

- (i) What is the effect of temperature on the ionic product of water? How will it change the pH value of a neutral solution?
- (ii) How many hours does it take to reduce 3 moles of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  with 2.0 A current intensity?
- (iii) How is urea prepared by Wohler synthesis?
- (iv) Two liquids A and B form type II non ideal solution which shows a minimum in its temperature -mole fraction plot (T- $\chi$  diagram). Can the two liquids be completely separated by fractional distillation?
- (v) The aqueous solution of sodium acetate is basic. Explain.

(d) Match the following: [5]

- |  |                              |
|--|------------------------------|
| (i) Disaccharide                         | (a) Lucas reagent            |
| (ii) Carbylamine                         | (b) Condensation polymer     |
| (iii) Dacron                             | (c) Obnoxious smell          |
| (iv) Low spin complex, $d^2sp^3$         | (d) Sucrose                  |
| (v) Anhydrous $\text{ZnCl}_2$ + conc.HCl | (e) Hexaamminecobalt(III)ion |

## PART II (50 Marks)

Answer six questions choosing two from Section A, two from Section B and two from Section C.

### SECTION A

Answer any two questions.

#### Question 2

- (a) (i) A solution containing 0.5 g of KCl dissolves in 100 g of water and freezes at  $-0.24^\circ\text{C}$ . Calculate the degree of dissociation of the salt. ( $K_f$  for water =  $1.86^\circ\text{C}$ )  
Atomic weights [K = 39, Cl = 35.5] [3]
- (ii) If 1.71 g of sugar (molar mass = 342) are dissolved in 500 ml of an aqueous solution at 300 K, what will be its osmotic pressure? [1]
- (iii) 0.70g of an organic compound when dissolved in 32g of acetone produces an elevation of  $0.25^\circ\text{C}$  in the boiling point. Calculate the molecular mass of organic compound ( $K_b$  for acetone =  $1.72 \text{ K kg mol}^{-1}$ ). [1]

- (b) (i) What is the difference between order of a reaction and the molecularity of a reaction? [2]
- (ii) A substance decomposes by following first order kinetics. If 50% of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose? [2]
- (c) Name the crystal structure of the copper metal. [1]

### Question 3

- (a) (i) Chromium metal crystallises with a body centered cubic lattice. The edge length of the unit cell is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in  $\text{g / cm}^3$ ? (atomic mass of Cr = 52.99) [2]
- (ii) Why does sodium chloride on heating with sodium vapours acquire yellow colour? [1]
- (iii) The equilibrium constant for the reaction: [1]
- $$\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})} \text{ at } 715 \text{ K, is } 6.0 \times 10^{-2}.$$
- If, in a particular reaction, there are  $0.25 \text{ mol L}^{-1}$  of  $\text{H}_2$  and  $0.06 \text{ mol L}^{-1}$  of  $\text{NH}_3$  present, calculate the concentration of  $\text{N}_2$  at equilibrium.
- (iv) Calculate the concentration of  $\text{OH}^-$  ions in solution when  $[\text{H}^+] = 6.2 \times 10^{-2} \text{ mol L}^{-1}$ . [1]
- (v) State the Le Chatelier's principle. [1]
- (b) For a crystal of sodium chloride, state: [2]
- (i) The type of lattice in which it crystallises.
- (ii) The coordination number of each sodium ion and chloride ion in the crystal lattice.
- (iii) The number of sodium ions and chloride ions present in a unit cell of sodium chloride.
- (iv) The structural arrangement of the sodium chloride crystal.
- (c) Consider the following reaction: [2]
- $$\text{N}_2\text{O}_{4(\text{g})} + \text{Heat} \rightleftharpoons 2\text{NO}_{2(\text{g})}$$
- How is the composition of equilibrium mixture affected by:
- (i) a change in temperature
- (ii) a change in pressure
- (iii) a change in concentration of  $\text{N}_2\text{O}_4$
- (iv) the removal of  $\text{NO}_2$  from the reaction mixture

#### Question 4

- (a) The specific conductance of a 0.01 M solution of acetic acid at 298 K is  $1.65 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The molar conductance at infinite dilution for  $\text{H}^+$  ion and  $\text{CH}_3\text{COO}^-$  ion are  $349.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and  $40.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively. Calculate: [3]
- (i) Molar conductance of the solution.
  - (ii) Degree of dissociation of  $\text{CH}_3\text{COOH}$ .
  - (iii) Dissociation constant for acetic acid.
- (b) (i) Calculate the e.m.f. of the following cell reaction at 298 K : [2]
- $$\text{Mg}_{(s)} + \text{Cu}^{2+} (0.0001 \text{ M}) \rightarrow \text{Mg}^{2+} (0.001 \text{ M}) + \text{Cu}_{(s)}$$
- The standard potential ( $E^0$ ) of the cell is 2.71 V.
- (ii) The solubility product ( $K_{sp}$ ) of  $\text{BaSO}_4$  is  $1.5 \times 10^{-9}$ . Calculate the solubility of barium sulphate in pure water and in 0.1 M  $\text{BaCl}_2$ . [2]
- (c) Explain following :
- (i) When  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  are added to a solution containing both,  $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  ions, which ion is precipitated first and why? [2]
  - (ii) Dissociation of  $\text{H}_2\text{S}$  is suppressed in acidic medium. [1]

### SECTION B

Answer any two questions

#### Question.5

- Write the IUPAC names of the following coordination compounds: [1]
- (i)  $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$
  - (ii)  $[\text{PtCl}_2(\text{NH}_3)_4][\text{PtCl}_4]$
- (b) State the hybridization and magnetic property of  $[\text{Fe}(\text{CN})_6]^{3-}$  ion according to the valence bond theory. [1]
- (c) (i) What type of isomers are  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ ? Give a chemical test to distinguish between them. [2]
- (ii) Write the structures of optical isomers of the complex ion  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  [1]

### Question 6

- (a) Give balanced chemical equations for the following reactions: [3]
- Fluorine is passed through cold, dilute NaOH solution
  - Hydrogen peroxide is treated with acidified  $\text{KMnO}_4$  solution.
  - Sulphuric acid is treated with hydrogen sulphide.
- (b) Draw the structure of xenon tetrafluoride molecule and state the hybridization of the central atom and the geometry of the molecule. [2]

### Question 7

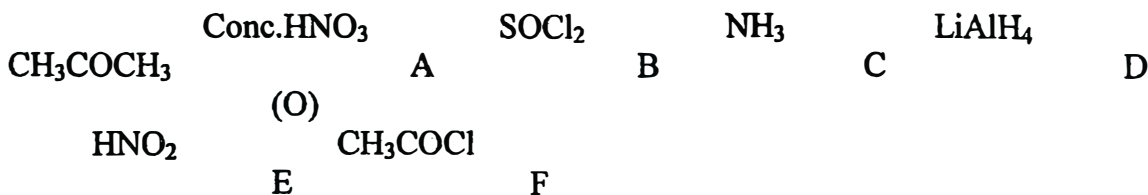
- (a) Name the important ore of silver. Write all the steps and reactions involved in the Cyanide process for the extraction of silver from its ore. [3]
- (b) Explain the following: [2]
- Why do transition metal ions possess a great tendency to form complexes?
- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases.

## SECTION C

Answer any two questions.

### Question 8

- [a] How can the following conversions be brought about:
- Glycerol to formic acid [1]
  - Chlorobenzene to phenol [1]
  - Diethyl ether to ethanol [1]
  - Phenol to aniline. [2]
- (b)
- How is iodohyform prepared from ethanol? Give balanced equation. [1]
  - What will be the product formed when chlorobenzene is heated with sodium metal in the presence of dry ether? [1]
- (c) Identify the compounds A, B, C, D, E and F: [3]



### Question 9

- (a) Give balanced equations for the following name reactions: [3]
- Reimer-Tiemann reaction.
  - Rosenmund reaction
  - Hoffmann's degradation reaction
- (b) Give one chemical test to distinguish between the following pairs of compounds: [3]
- Ethylamine and diethylamine.
  - Acetaldehyde and benzaldehyde
- (c) (i) Arrange the following compounds in the ascending order of their basic strength and give reasons for your answer: [2]  
Methylamine, Aniline, Ethylamine, Diethyl ether
- (ii) Name the monomers and the type of polymerization in each of the following polymers: [2]
- Polyester
  - Bakelite

### Question 10

- (a) An organic compound A with molecular formula  $C_2H_7N$  on reaction with nitrous acid gives a compound B. B on controlled oxidation gives compound C. C reduces Tollen's reagent to give silver mirror and D. B reacts with D in the presence of concentrated sulphuric acid to give sweet smelling compound E. Identify A, B, C, D and E. Give the reaction of C with ammonia. [3]
- (b) Give balanced equations for the following reactions: [4]
- How will you convert ethyl amine to methyl amine?
  - What is the effect of denaturation on the structure of proteins?
  - Name the nitrogen base residues present in DNA.
- (c) Give balanced equations for the following reactions: [3]
- Aniline is treated with nitrous acid and HCl at low temperature.
  - Acetyl chloride is treated with ethyl alcohol.
  - Formaldehyde is treated with ammonia