

Q.P. Code : **12863**

(2½ Hours)

[ Total Marks : 75

- N.B. : (1) All questions are compulsory.  
 (2) Figures to the right indicate full marks.  
 (3) Use of Logarithmic tables/Non-programmable calculator is allowed.  
 (4) Answers to the two sections must be written in two separate answer books and tied together.

Physical Constants :-

$$N = 6.022 \times 10^{23}$$

$$K = 1.38 \times 10^{-23} \text{ J/K}$$

$$F = 96500 \text{ C}$$

$$R = 8.314 \text{ J/mol/K}$$

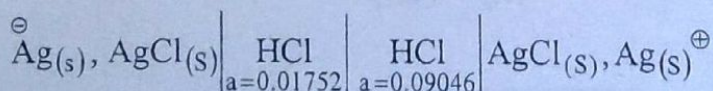
$$h = 6.625 \times 10^{-34} \text{ Js}$$

$$c = 3.0 \times 10^8 \text{ m/s}$$

$$\frac{2.303 RT}{F} = 0.0592 \text{ at } 298 \text{ K}$$

### SECTION - I

- Attempt any **three** of the following.
  - By how much would the normal boiling point 353.1 K be raised on dissolving 1.2g of n-hexane ( $C_6H_{14}$ ) in 100 g of benzene. Ebullioscopic constant of benzene is  $2.62 \text{ k kg mol}^{-1}$ . 5
  - With a neat labelled diagram, explain application of phase rule to water system. 5
  - (i) State and explain the Raoult's law. 2  
 (ii) Show graphically the elevation in boiling point of a solvent due to addition of non volatile solute. 3
  - Derive Vant' Hoff's equation for osmotic pressure. 5
  - What do you understand by eutectic point? Explain the phase diagram of lead-silver system. 5
  - Describe the salient features of a triangular phase diagram for three component system. 5
- Attempt any **three** of the following.
  - Calculate the ionic strength of the solution containing  $0.01 \text{ mol.dm}^{-3} \text{ Zn Cl}_2$  and  $0.2 \text{ mol.dm}^{-3}$  of  $\text{FeCl}_3$ . 5
  - Derive an expression for the emf of an electrolyte concentration cell without transference reversible to anion. 5
  - Calculate the liquid junction potential of the following cell 5



if the transport number of  $H^+$  is 0.83 at 298 K.

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- (D) Describe how the solubility product of a sparingly soluble salt can be determined by using a chemical cell. 5
- (E) State any three merits and any two demerits of the glass electrode. 5
- (F) What is a salt bridge? Where is it used? What are its functions? 5

3. (A) State true or false :- 4

- (i) When two solutions have same osmotic pressure at a given temperature they are said to be isotonic.
- (ii)  $\text{CaCO}_3$  system is a typical example of a one component system.
- (iii) Osmotic pressure of a solution is a colligative property.
- (iv) At triple point  $F = 1$

OR

(A) Fill in the blanks with correct alternative. 4

- (i) Mathematical expression of Gibb's phase rule is \_\_\_\_\_. ( $F = C - P + 2$ ,  $F = C + P - 2$ ,  $F = C - P + 1$ )
- (ii) When solute particles associate 'i' is \_\_\_\_\_ unity. (equal to, less than, greater than)
- (iii) When a non volatile solute is dissolved in a solvent, vapour pressure of the solvent \_\_\_\_\_ (decreases, increases, remains same)
- (iv) Sulphur exist in \_\_\_\_\_ phases. (two, three, four)

(B) State true or false. 4

- (a) Quinhydrone contains equimolar amount of quinone and hydroquinone.
- (b) According to Debye Huckal limiting law  $\log \gamma = AZ_i^2 \sqrt{\mu}$
- (c) In chemical cell, the emf is due to a chemical reaction occurring within the cell.
- (d)  $\text{Pt}, \text{H}_2(\text{g}) | \underset{\text{aq}}{\text{HCl}} | \text{AgCl}(\text{s}), \text{Ag}$

is an example of a concentration cell.

OR

(b) Match the following :- 4

- |                                  |                                |
|----------------------------------|--------------------------------|
| (a) $\text{CuSO}_4$              | (i) $108 \text{ m}^5 \gamma^5$ |
| (b) $\text{K}_2\text{SO}_4$      | (ii) $4 \text{ m}^2 \gamma^2$  |
| (c) $\text{Na}_3\text{PO}_4$     | (iii) $9 \text{ m}^2 \gamma^4$ |
| (d) $\text{Al}_2(\text{SO}_4)_3$ | (iv) $\text{m}^2 \gamma^2$     |
|                                  | (v) $27 \text{ m}^4 \gamma^4$  |
|                                  | (vi) $4 \text{ m}^3 \gamma^3$  |



## SECTION - II

4. Answer any **three** of the following.

- (A) Explain the following terms giving one example for each 5  
 (i) Proper rotation axis (ii) Mirror plane  
 (B) Explain the point group assigned to water molecule. 5  
 (C) Explain (i) Importance of molecular symmetry 2  
 (ii) Inversion centre 3  
 (D) Define 'Point group'. Explain point group assigned to trans dichloro ethylene. 5  
 (E) Draw the molecular orbital diagram for  $\text{BeH}_2$  molecule. Explain its magnetic property. 5  
 (F) What is Walsh correlation diagram ? Explain its use in the determination of structure of  $\text{H}_3^+$  ion 5

5. Answer any **three** of the following.

- (A) What are the oxoanions ? How are they classified ? 5  
 (B) Give the hydrolysis reactions of  $\text{Cr}^{3+}$  ions in aqueous medium. 5  
 (C) Write Latimer equation ? Explain its significance. 5  
 (D) What is predominance diagram ? Explain predominance diagram for (i) strongly basic anions (ii) weakly basic anions. 5  
 (E) Explain Acidic Basic and Amphoteric solvents with suitable examples. 5  
 (F) With respect to liquid  $\text{N}_2\text{O}_4$  as solvent answer the following : 5  
 (i) Auto ionization reaction  
 (ii) Reactions with metals  
 (iii) Acid base reactions

6. Answer the following :

(A) Select and write the most appropriate answer.

- (a) Doing nothing operation is same as \_\_\_\_\_.  
 (i) centre of symmetry (ii) identity (iii) reflection  
 (b) In ammonia molecule the principal axis is \_\_\_\_\_ axis.  
 (i)  $C_2$  (ii)  $C_3$  (iii)  $C_4$   
 (c) Point group assigned to HCl is \_\_\_\_\_.  
 (i)  $D_{\infty h}$  (ii)  $C_{2v}$  (iii)  $C_{\infty v}$   
 (d) Photo electron spectrum of water molecule shows \_\_\_\_\_ bands  
 (i) 2 (ii) 3 (iii) 4

OR

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(A) State whether the following statements are True or False.

(p) Water is linear molecule.

(q) Point group assigned to  $H_2$  molecule is  $C_{2v}$

(r) Order of point group  $D_{3h}$  is 6.

(s) On the basis of symmetry symbol 't' denotes triply degenerate orbitals.

(B) Select and write the most appropriate answer.

(a) \_\_\_\_\_ is non ionizing solvent

(i) HF

(ii)  $NH_3$

(iii)  $C_6H_6$

(b) In auto ionization of liquid  $NH_3$ , species not obtained is \_\_\_\_\_.

(i)  $NH_4^+$

(ii)  $NH_2^-$

(iii)  $N^{4-}$

(c) As the number of oxo groups increases basicity \_\_\_\_\_.

(i) increases

(ii) decreases

(iii) does not change.

OR

(B) State whether the following statements are TRUE or FALSE.

(p)  $CCl_4$  is ionizing solvent

(q) Liquid  $CH_3COOH$  exist as dimer.

(r) Dilute solution of sodium metal in liquid  $NH_3$  is green in colour.

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