

Duration: 2 1/2 hrs.

Marks: 75

- N.B. 1. All questions are compulsory.  
 2. Figures to the right indicate full marks.  
 3. Use of log tables / non-programmable calculator is allowed.  
 4. Answers to the two sections must be written in separate answer books and submitted separately

Physical constants:

$N=6.022 \times 10^{23}$	$h=6.626 \times 10^{-34} \text{ J s}$	$\frac{2.303 R T}{F} = 0.05916 \text{ at } 298\text{K}$
$F=96500 \text{ C}$	$k=1.38 \times 10^{-23} \text{ J K}^{-1}$	$F$
$R=8.314 \text{ J/K/mol}$	$c= 3 \times 10^8 \text{ m/s}$	$\pi= 3.142$

**SECTION-I**

1. Attempt **any three** of the following:

- (A) What is condensed phase rule? Explain its application to lead-silver system. 5  
 (B) Explain the application of phase rule to sulphur system. 5  
 (C) Define (i) Phase (ii) Number of components (iii) Degree of freedom. 5  
 (D) Derive Van't Hoff's equation for Osmotic pressure. 5  
 (E) Derive the equation  $\Delta T_f = K_f \cdot m$  5  
 (F) A solution containing 3 g solute in 60 g of water gave boiling point elevation of 0.2. If  $K_b$  is  $0.512 \text{ K kg mol}^{-1}$ , calculate the molecular weight of the solute. 5

2. Attempt **any three** of the following:

- (A) Derive an expression for emf of electrode concentration cell reversible to cation. 5  
 (B) Explain the use of glass electrode for determination of pH of a solution. 5  
 (C) Explain the origin of liquid junction potential. 5  
 (D) Derive an expression for electrolyte concentration without transference reversible to cation. 5  
 (E) Calculate the mean activity coefficient of 0.2m  $\text{CaCl}_2$ . (A=0.509) 5  
 (F) The emf of the cell  $\text{SCE} \parallel \text{solution saturated with QH} \mid \text{Pt}$  is 0.350 V at 298K . Calculate the pH of the solution. 5

3. (A) State true or false

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- (a) For NaCl Vant Hoff's factor  $i > 1$
- (b)  $\Delta T_b$  is elevation of boiling point.
- (c) In water system, at triple point  $F=0$ .
- (d) Pure lead melts at 600K.

OR

(A) Match the following

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- |                          |                                   |
|--------------------------|-----------------------------------|
| (p) Osmosis              | (i) Ebullioscopic constant        |
| (q) $k_b$                | (ii) semipermeable membrane       |
| (r) One component system | (iii) lowering of vapour pressure |
| (s) Ternary system       | (iv) Water system                 |
|                          | (v) plait point                   |

3. (B) State true or false:

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- (a) Reduction is gain of electrons.
- (b) For 1:1 type of electrolyte  $a = m^2 \gamma^2$
- (c) Salt bridge contains  $KNO_3$
- (d) For ideal solution  $a = m$

OR

(B) Match the following.

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- |                               |                         |
|-------------------------------|-------------------------|
| (p) Lead storage cell         | (i) KCl                 |
| (q) Uni-univalent electrolyte | (ii) Galvanic cell      |
| (r) Glass electrode           | (iii) $Q / H_2Q = 1$    |
| (s) Quinhydrone electrode     | (iv) colloidal solution |
|                               | (v) Gas electrode       |

## SECTION-II

4. Attempt any three of the following:

- (A) Explain  $C_{3v}$  and  $C_{\infty v}$  point groups with a suitable example for each. 5
- (B) Explain, giving a suitable example, the  $D_{\infty h}$  point group. 5
- (C) Explain the following symmetry elements with a suitable example for each: 5
- (i) Identity
  - (ii) Centre of symmetry
- (D) Discuss the symmetry operations and assign the point group to  $BCl_3$  molecule. 5
- (E) Draw a neat labelled molecular orbital diagram for  $BeH_2$  molecule, showing the distribution of electrons in various energy levels. 5
- (F) Give the wave equations for the formation of molecular orbitals in trihydrogen ion and draw a neat labelled molecular orbital diagram for triangular  $H_3^+$  ion. 5

5. Attempt **any three** of the following:

- (A) Explain the hydrolysis reactions of  $Cr^{3+}$  ion using predominance diagrams 5
- (B) Explain the process of hydration of monoatomic cation. How does it render acidity to aqueous solution? 5
- (C) Discuss the classification of oxoanions. 5
- (D) What are ionizing and non-ionizing solvents? Explain with suitable examples 5
- (E) With reference to liquid  $N_2O_4$  as solvent, explain the following with balanced equations. 5
- (i) Autoionization reactions.
  - (ii) Redox reactions
  - (iii) Acid base reactions
- (F) Write a note on 'metal ammonia solutions' 5

6. Attempt the following:

(A) Select and write the appropriate answer.

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(a) H<sub>2</sub>O molecule shows \_\_\_\_\_ axis of proper rotation.

- (i) C<sub>1</sub>                                      (ii) C<sub>2</sub>                                      (iii) C<sub>3</sub>

(b) A reflection which contains the principal axis is called \_\_\_\_\_ plane.

- (i) vertical                                      (ii) horizontal                                      (iii) dihedral

(c) Point group assigned to trans dichloroethylene molecule is \_\_\_\_\_.

- (i) D<sub>2h</sub>                                      (ii) C<sub>3h</sub>                                      (iii) C<sub>2h</sub>

(d) On the basis of symmetry rules, label 'a' denotes \_\_\_\_\_ degenerate orbitals.

- (i) triply                                      (ii) doubly                                      (iii) non

**OR**

(A) State whether the following statements are **true** or **false**.

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(p) A molecule having a C<sub>n</sub> axis and nC<sub>2</sub> axes perpendicular to it belongs to C<sub>n</sub> point group.

(q) Allene molecule possess dihedral plane.

(r) The plane perpendicular to the principal axis is called vertical plane.

(s) BeH<sub>2</sub> and H<sub>2</sub>O molecules have same structure as they have same number of peripheral atoms.

(B) Select and write the appropriate answer.

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(a) pH range for weakly acidic cations is between \_\_\_\_\_.

- (i) 6 and 11.5                                      (ii) 11.5 and 14                                      (iii) 1 to 6

(b) One of the products of autoionisation of acetic acid is \_\_\_\_\_.

- (i) CH<sub>3</sub>CO<sup>+</sup>                                      (ii) CH<sub>3</sub>COO<sup>-</sup>                                      (iii) CH<sub>3</sub><sup>+</sup>

(c) \_\_\_\_\_ among the following is a protonic solvent.

- (i) CCl<sub>4</sub>                                      (ii) SO<sub>2</sub>                                      (iii) H<sub>2</sub>O

OR

(B) State whether the following statements are **true or false**.

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(p) Using Latimer's equation, hydration energy of cations can be calculated.

(q) The basicity of oxoanions increases with increasing number of oxo groups.

(r)  $\text{CH}_3\text{COOH}$  in liquid  $\text{NH}_3$  acts as a weak acid.

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