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:  $N=6.022 \times 10^{23}$  $h=6.626 \times 10^{-34} \text{ J s}$ 2.303 R T = 0.05916 at 298 K $k=1.38 \times 10^{-23} \text{ J K}^{-1}$ F=96500 C F  $c = 3x \cdot 10^8 \text{ m/s}$  $\pi = 3.142$ R=8.314 J/K/mol SECTION-I 1. Attempt any three of the following: (A) Explain the phase diagram of lead-silver system. 5 (B) Explain the application of phase rule to water system. 5 (C) Explain the terms binodal curve and plait point. 5 (D) Derive the equation  $\pi . V = n R T$ 5 (E) Derive the equation  $\Delta T_e = K_b .m$ 5 (F) A solution containing 2 g solute in 80 g of water gave boiling point elevation 5 of 0.2 If K<sub>b</sub> is 0.512 K kg mol<sup>-1</sup>, calculate the molecular weight of the solute. 2. Attempt **any three** of the following: (A) Derive an expression for emf of electrode concentration cell reversible to anion. 5 (B) Explain the use of quinhydrone electrode for determination of pH of a solution. 5 (C) What is liquid junction potential? How is it eliminated? 5 (D) Explain (i) ionic strength (ii) Debye-Huckel limiting law 5 (E)Calculate the mean activity coefficient of 0.3m Na<sub>2</sub>SO<sub>4</sub>. 5 (A=0.509)

Q. P. Code: 38694 (F) Calculate emf of the cell Ag / AgNO<sub>3</sub>  $AgNO_3 / Ag$ m=0.01m = 0.1 $\gamma = 0.50$  $\gamma = 0.85$ if transport number of silver is 0.46. 3. (A) State true or false (a) For ideal solution Vant Hoff's factor is 1. (b)  $\Delta T_f$  is depression of freezing point. (c) Sulphur exits in four phases. (d) Ternary system is expressed by triangular phase diagram OR (A)Match the following 4 (p) Raoult's law (i) Cryoscopic constant  $(q) k_f$ (ii) π (r) One component system (iii) lowering of vapour pressure (iv) Sulphur system (s) Ternary system (v) Acetone-water-phenol 3. (B) State true or false: 4 (a) Oxidation is loss of electrons. (b)  $a=m. \gamma$ (c) Salt bridge contains agar-agar. (d) All glass electrodes do not have same  $E^0_G$ . OR (B) Match the following. 4 (p) Galvanic cell (i) µ (q) Ionic strength (ii) Daniel cell (r) Glass electrode (iii) pH range 1-8 (s) Quinhydrone electrode (iv) ion-selective (v) SCE

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## **SECTION-II**

4. Attempt any three of the following:	2007
(A) Explain $C_{2v}$ and $C_{\infty v}$ point groups, giving suitable examples.	5
(B) Explain the following with a suitable example:	
(i) Inversion Centre	222
(ii) Improper rotational axis	5.2.5.6 4.0.6
(C) Identify the symmetry elements and assign the point group to BCl₃ molecule.	2002
(D) Discuss the symmetry operations and assign the point group to H₂ molecule.	5
(E) Give the wave equations for the formation of molecular orbitals in BeH₂ molecule. (MO diagram not expected)	5
(F) Draw a neat labelled molecular orbital diagram for H₂O molecule, showing the distribution of electrons in various energy levels.	5
5. Attempt <b>any three</b> of the following:	
(A) Define Hydration energy. Explain the hydration of cation and anion in	5
an aqueous medium.	
(B) What are predominance diagrams? Explain the predominance diagrams	5
for (a) Weakly acidic cations, (b) Strongly acidic cations.	
(C) Write a note on `polyatomic anions'.	5
(D) Explain (i) acidic, (ii) basic, (iii) amphiprotic solvents with suitable examples.	5
(E) With reference to liquid NH₃ as solvent, explain the following with	5
balanced equations.	
(i) Autoionization reactions.	
(ii) Redox reactions	
(iii) Acid base reactions	
(F) Justify the following statements:	5
(a) Solvents with high dielectric constant are better solvents for ionic compounds.	
(b) Dipole moment of acetic acid is zero.	

6. Attempt the following:			
(A) Select and write the appro	opriate answer.		
(a) The operation that leaves (i) centre of symmetry	the molecule unchana (ii) identity	ged is called (iii) centre of gravity	
(b) The order of the rotationa (i) 1	al axis in H₂O molecule (ii) 2	is	
(c) Point group assigned to N	H₃ molecule is		30
(i) C <sub>2v</sub>	(ii) C <sub>3v</sub>	(iii) C <sub>2h</sub>	
(d) Structure of H <sub>3</sub> <sup>+</sup> ion is			
(i) linear	 (ii) planar triangular	(iii) tetrahedral	
	OR		
(A) State whether the followi	ng statements are <b>tru</b>	e or false.	2
(p) Symmetry element identif	ty is denoted by the sy	ymbol I.	
(q) Trans dichloroethylene m	olecule possess dihed	ral plane of symmetry.	
(r) A group is a collection of s certain rules.	ymmetry elements wl	nich are related to one another by	
(s) Water molecule shows tw	o bands in its photoel	ectron spectrum.	
6.(B) Select and write the ap	propriate answer.		3
(a) The anions with $pK_b$ va	alues between	are weakly basic anions.	
(i) -4 and 1	(ii) 1 and 6	(iii) 6 and 11.5	
(b) One of the products o	f autoionization react	ion of dinitrogen tetraoxide is	
(i) NO <sup>+</sup>	(ii) NO₂	(iii) NO <sub>3</sub> <sup>2-</sup>	
(c) Dilute solution of met	cal ammonia show	conductivity.	
(i) low	(ii) high	(iii) no	
	OR		
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- (B) State whether the following statements are **true or false**.
  - (p) Hydrolysis of hydrated cation renders the solution basic.
  - (q) Ionising solvents are non polar in nature.
  - (r) Liquid N<sub>2</sub>O<sub>4</sub> is a poor solvent for ionic compounds.

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