

Total No. of Printed Pages—12

**4 SEM TDC CHM M 1 (N/O)**

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( May )

**CHEMISTRY**

( Major )

Course : 401

**( Physical Chemistry )**

*The figures in the margin indicate full marks  
for the questions*

( New Course )

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Select the correct answer : 1×5=5

(a) The number of electrons involved in the reaction when one faraday of electricity is passed through the electrolyte is

(i)  $12 \times 10^{46}$

(ii) 96500

(iii)  $6 \times 10^{23}$

(iv)  $8 \times 10^{16}$

**8P/683**

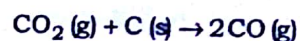
**( Turn Over )**

( 2 )

- (b) The increase in the molar conductivity of HCl with dilution is due to
- (i) decrease in interionic forces
  - (ii) increase in self-ionization of water
  - (iii) hydrolysis of water
  - (iv) decrease in self-ionization of water
- (c) For an electrolytic solution of  $0.05 \text{ mol l}^{-1}$ , specific conductivity is  $0.0110 \text{ S cm}^{-1}$ . The molar conductivity (in  $\text{S cm}^2 \text{ mol}^{-1}$ ) is
- (i) 0.055
  - (ii) 55
  - (iii) 220
  - (iv) 0.22
- (d) The potential of hydrogen electrode having  $\text{pH} = 10$  is
- (i) 0.592 V
  - (ii) -0.0592 V
  - (iii) -0.592 V
  - (iv) None of the above

( 3 )

- (e) For the reaction between  $\text{CO}_2(\text{g})$  and graphite

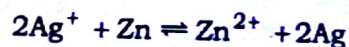


$\Delta H = +170.0 \text{ kJ}$  and  $\Delta S = 170 \text{ JK}^{-1}$ . The reaction is spontaneous at

- (i) 1200 K
- (ii) 900 K
- (iii) 500 K
- (iv) 298 K

2. Answer any five questions from the following : 2×5=10

- (a) Describe any two factors upon which the transport number of an ion depends.
- (b) Distinguish a reversible cell from an irreversible cell.
- (c) Explain how the conductance of an electrolyte depends upon the viscosity of the medium.
- (d) For the electrochemical cell



$E^\circ$  cell is 1.56 V at 25 °C. Calculate the equilibrium constant of the reaction.

( Continued 8P/683

( Turn Over )



( 4 )

- (e) Prove that for a system, decrease in the Helmholtz free energy function at constant temperature and volume represents the maximum amount of work obtainable from the system.
- (f) One mole of an ideal gas expands isothermally and reversibly from  $5 \text{ dm}^3$  to  $10 \text{ dm}^3$  at 300 K. Calculate  $\Delta G$  and  $\Delta A$ .

UNIT—I

3. Answer any two of the following questions :  $4\frac{1}{2} \times 2 = 9$

- (a) For one mole of an ideal gas, prove that

$$\overline{\Delta S} = \overline{C}_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad 4\frac{1}{2}$$

- (b) (i) Prove that

$$\left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T \quad 2\frac{1}{2}$$

- (ii) State and explain Nernst's heat theorem. 2

- (c) (i) For a reaction  $\Delta G = -a + bT \ln T$ , where  $a$  and  $b$  are constants. Express  $\Delta H$  as a function of  $T$ . 2

8P/683

( Continued 8P/683

( 5 )

- (ii) Calculate  $\Delta G$  for the formation of  $\text{H}_2\text{O}(\text{l})$  from the elements at  $25^\circ\text{C}$ ,  $\Delta H_f^\circ(\text{H}_2\text{O}) = -286 \text{ kJ}$ . Entropies of  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are respectively  $130.6 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $205.0 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $70.3 \text{ JK}^{-1} \text{ mol}^{-1}$ . 2

UNIT—II

4. Answer any two of the following questions :  $7 \times 2 = 14$

- (a) (i) What is transport number? Derive the relation between ionic conductance and transport number. 1+3=4

- (ii) The equivalent conductance of a very dilute solution of  $\text{NaNO}_3$  at  $18^\circ\text{C}$  is  $210.4 \text{ ohm}^{-1} \text{ cm}^2$ . If the ionic conductance of  $\text{NO}_3^-$  ion in the solution is  $122.14 \text{ ohm}^{-1} \text{ cm}^2$ , calculate the transport number of  $\text{Na}^+$  ion in the solution. 3

- (b) (i) Represent the variation of equivalent conductances of  $\text{KCl}$  and  $\text{CH}_3\text{COOH}$  with dilution graphically and give an explanation for such variation. 4

- (ii) Describe briefly Wien effect and Debye-Falkenhagen effect. 3

( Turn Over )

- (c) (i) State and explain Kohlrausch's law of independent migration of ions. 3

(ii) Calculate the equivalent and molar conductances of aqueous  $\text{BaSO}_4$  solution at infinite dilution. Given,

$$\Lambda_{\frac{1}{2}\text{Ba}(\text{NO}_3)_2}^\circ = 135.04 \times 10^{-4} \Omega^{-1} \text{m}^2 \text{equiv}^{-1}$$

$$\Lambda_{\frac{1}{2}\text{H}_2\text{SO}_4}^\circ = 429.60 \times 10^{-4} \Omega^{-1} \text{m}^2 \text{equiv}^{-1}$$

$$\Lambda_{\text{HNO}_3}^\circ = 421.24 \times 10^{-4} \Omega^{-1} \text{m}^2 \text{equiv}^{-1} \quad 4$$

### UNIT—III

5. Answer any two of the following questions :  $5 \times 2 = 10$

(a) (i) Discuss any two types of electrode used in galvanic cells. 3

(ii) Write the difference between electrode concentration cell and electrolytic concentration cell. 2

(b) (i) Discuss how the pH of a solution can be measured with the help of a quinhydrone electrode. 3

(ii) Describe how the e.m.f. is generated in a hydrogen-oxygen fuel cell. 2

- (c) (i) Derive a relation between the electromotive force and the equilibrium constant of a cell reaction. 3

(ii) Aluminium oxide may be electrolysed at  $1000^\circ\text{C}$  to furnish aluminium metal. The cathode reaction is



Calculate the amount of electricity to produce 5.12 kg of aluminium by this method. 2



( 8 )

( Old Course )

Full Marks : 48  
Pass Marks : 19

Time : 3 hours

1. Select the correct answers :

1×5=5

(a) Which of the following ions possesses maximum ionic mobility?

- (i)  $\text{Na}^+$
- (ii)  $\text{K}^+$
- (iii)  $\text{H}^+$
- (iv)  $\text{OH}^-$

(b) The unit of cell constant is

- (i)  $\text{ohm}^{-1} \text{cm}^{-1}$
- (ii)  $\text{cm}^{-1}$
- (iii)  $\text{ohm}^{-1}$
- (iv)  $\text{ohm}^{-1} \text{cm}$

(c) Electrode potential of a standard hydrogen electrode is

- (i) 1.0 V
- (ii) 0 V
- (iii) -1.0 V
- (iv) 0.5 V

8P/683

( Continued )

8P/683

( 9 )

(d) Which of the following is an example of reversible cell?

- (i) Fuel cell
- (ii) Dry cell
- (iii) Lead storage cell
- (iv) Electrolytic cell

(e) The value of activity coefficient for an ideal gas is

- (i) 1
- (ii)  $> 1$
- (iii)  $< 1$
- (iv) None of the above

2. Answer the following questions : 2×5=10

(a) Explain why  $\text{H}^+$  and  $\text{OH}^-$  have exceptionally high ionic mobilities in aqueous solution. 2

(b) State Kohlrausch's law. Why is this law applicable only at infinite dilution? 1+1=2

(c) Explain how electrode potential of an electrode is measured. 2

(d) Explain why quinhydrone electrode is not suitable to measure the pH of strongly basic solution. 2

(e) Define chemical potential. What is its physical significance? 1+1=2

( Turn Over )



( 10 )

3. Answer any two of the following questions :

7×2=14

- (a) (i) Define transference number of ions. Derive the relationship between transference number and ionic velocities. 1+3=4
- (ii) Discuss moving boundary method for determination of transference number of ions. 3
- (b) (i) Explain Debye-Hückel concept of ionic atmosphere. Explain the variation of molar conductance with concentration for strong electrolytes with the help of asymmetry effect. 2+2=4
- (ii) What do you mean by conductometric titration? Discuss the advantages of conductometric titration over volumetric titration. 1+2=3
- (c) (i) State and explain Walden's rule. Why is this rule not valid for small ions? 2+1=3
- (ii) Explain how solubility and solubility product of a sparingly soluble salt can be measured from conductometric measurements. 3

8P/683

( Continued )

( 11 )

- (iii) The conductivity of a decinormal solution of KCl at 298 K is  $0.0112 \text{ ohm}^{-1} \text{ cm}^{-1}$ . The resistance of the cell containing the solution was found to be 55 ohm. Calculate the cell constant. 1

4. Answer any two of the following questions :

5×2=10

- (a) What is glass electrode? Describe how it can be used to measure the pH of a solution. What do you mean by asymmetry potential of glass electrode? 1+3+1=5
- (b) (i) Derive an expression relating e.m.f. of a cell with the concentration of the reactants and products of the cell reaction. 3
- (ii) A copper sulphate solution was electrolysed for one hour resulting in the deposition of 0.5 g copper on cathode. What was the current strength? (Atomic weight of Cu = 63.57 u) 2
- (c) What are fuel cells? Draw the schematic diagram of  $\text{H}_2\text{-O}_2$  fuel cell. Discuss how e.m.f. is generated in a  $\text{H}_2\text{-O}_2$  fuel cell. 1+1+3=5

8P/683

( Turn Over )

5. Answer any three of the following questions :

3×3=9

- (a) With the help of Le Chatelier principle, work out the condition which would favour the maximum yield of ammonia in the reaction



$$\Delta H = -92.38 \text{ kJ}$$

- (b) Derive van't Hoff equation in the form

$$\frac{d(\ln k_p)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

- (c) Derive Duhem-Margules equation.

- (d) Discuss the effects of temperature and pressure on chemical potential.

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