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4 SEM TDC CHM M 1 (N/O)

2018

(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) 12×10^{46}

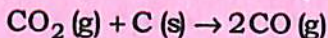
(ii) 96500

(iii) 6×10^{23}

(iv) 8×10^{16}

- (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 mol l^{-1} , specific conductivity is 0.0110 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

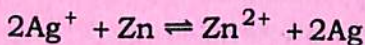
- (e) For the reaction between $\text{CO}_2(\text{g})$ and graphite



$\Delta H = +170.0 \text{ kJ}$ 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° cell is 1.56 V at 25 °C. Calculate the equilibrium constant of the reaction.

- (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 dm^3 to 10 dm^3 at 300 K. Calculate ΔG and ΔA .

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 ΔH as a function of T . 2\frac{1}{2}

- (ii) Calculate ΔG for the formation of $\text{H}_2\text{O}(\text{l})$ from the elements at 25°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 :

7×2=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 NaNO_3 at 18°C is $210.4 \text{ ohm}^{-1} \text{ cm}^2$. If the ionic conductance of NO_3^- ion in the solution is $122.14 \text{ ohm}^{-1} \text{ cm}^2$, calculate the transport number of Na^+ ion in the solution. 3
- (b) (i) Represent the variation of equivalent conductances of KCl and CH_3COOH with dilution graphically and give an explanation for such variation. 4
- (ii) Describe briefly Wien effect and Debye-Falkenhagen effect. 3

- (c) (i) State and explain Kohlrausch's law of independent migration of ions. 3
- (ii) Calculate the equivalent and molar conductances of aqueous 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

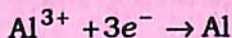
5. Answer any *two* of the following questions :

5×2=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

(7)

- (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 °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

(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) Na^+

(ii) K^+

(iii) H^+

(iv) OH^-

(b) The unit of cell constant is

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

(ii) cm^{-1}

(iii) 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

(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 H^+ and 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

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

- (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

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

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

- (c) Derive Duhem-Margules equation.
- (d) Discuss the effects of temperature and pressure on chemical potential.

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