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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}

(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 mol l^{-1} , specific conductivity is 0.0110 S cm^{-1} . The molar conductivity (in $\text{S cm}^2 \text{ mol}^{-1}$) is

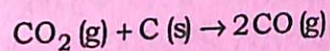
- (i) 0.055
- (ii) 55
- (iii) 220
- (iv) 0.22

(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

(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

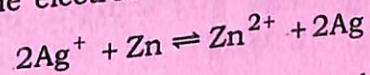
2. Answer any five questions from the following : 2×5=10

(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° cell is 1.56 V at 25°C . Calculate the equilibrium constant of the reaction.

(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 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

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

- (b) (i) Prove that

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

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

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

(5)

- (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 $70.3 \text{ JK}^{-1} \text{ mol}^{-1}$.

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 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

(Turn Over)

(6)

- (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,

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

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

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

UNIT—III

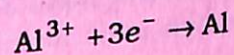
5. Answer any two of the following questions : 5×2=10

- (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. 2
(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