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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 $0 \cdot 05 \text{ mol l}^{-1}$, specific conductivity is $0 \cdot 0110 \text{ S cm}^{-1}$. 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 pH = 10 is

(i) 0·592 V

(ii) − 0·0592 V

(iii) − 0·592 V

(iv) None of the above

(Continued

(e) For the reaction between $CO_2(g)$ and graphite

$$CO_2(g) + C(s) \rightarrow 2CO(g)$$

$\Delta H = +170 \cdot 0$ 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

$$2Ag^+ + Zn \rightleftharpoons Zn^{2+} + 2Ag$$

$E°$ cell is 1·56 V at 25 °C. Calculate the equilibrium constant of the reaction.

(Turn Over)

(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 : $4\frac{1}{2}\times2=9$

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

$$\overline{\Delta S} = \overline{C}_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$ 4½

(b) (i) Prove that

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$ 2½

(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. 2½

(ii) Calculate ΔG for the formation of H_2O (l) from the elements at 25 °C, $\Delta H^{\circ}_{f(H_2O)} = -286$ kJ. Entropies of H_2 (g), O_2 (g) and H_2O (l) are respectively 130·6 JK^{-1} mol^{-1}, 205·0 JK^{-1} mol^{-1} and 70·3 JK^{-1} mol^{-1}. 2

UNIT—II

4. Answer any *two* of the following questions : $7\times2=14$

(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 ohm^{-1} cm^2. If the ionic conductance of NO_3^- ion in the solution is 122·14 ohm^{-1} 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)

(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,

$\overset{\circ}{\wedge}_{\frac{1}{2}Ba(NO_3)_2} = 135 \cdot 04 \times 10^{-4}\ \Omega^{-1}\ m^2\ equiv^{-1}$

$\overset{\circ}{\wedge}_{\frac{1}{2}H_2SO_4} = 429 \cdot 60 \times 10^{-4}\ \Omega^{-1}\ m^2\ equiv^{-1}$

$\overset{\circ}{\wedge}_{HNO_3} = 421 \cdot 24 \times 10^{-4}\ \Omega^{-1}\ m^2\ equiv^{-1}$ 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.

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

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

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

(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

$$Al^{3+} + 3e^- \rightarrow Al$$

Calculate the amount of electricity to produce 5·12 kg of aluminium by this method. 2

(Turn Over)