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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 $0 \cdot 05\ mol\ l^{-1}$, specific conductivity is $0 \cdot 0110\ S\ cm^{-1}$. The molar conductivity (in $S\ cm^2\ mol^{-1}$) 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 $\Delta S = 170$ 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.

(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 : 4½×2=9

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

$$\overline{\Delta S} = \overline{C}_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$ 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. 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. 2½

(Continued)

(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 : 7×2=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 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

(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 : 5×2=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 °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

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

(ii) cm^{-1}

(iii) ohm^{-1}

(iv) ohm^{-1} 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

(Continued)

(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

(Continued)

(iii) The conductivity of a decinormal solution of KCl at 298 K is $0{\cdot}0112\ ohm^{-1}\ cm^{-1}$. 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 H_2-O_2 fuel cell. Discuss how e.m.f. is generated in a H_2-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

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g);$$

$$\Delta H = -92 \cdot 38 \text{ kJ}$$

(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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