4 SEM TDC CHMH (CBCS) C 10

2022

(June/July)

CHEMISTRY

(Core)

Paper : C–10

(Physical Chemistry)

Full Marks : 53

Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×4=4

(a) The relation between equivalent conductance (Λ_e) and molar conductance (Λ_m) for $Al_2(SO_4)_3$ is

(i) $\Lambda_e = \Lambda_m$

(ii) $\Lambda_e = \frac{1}{2}\Lambda_m$

(iii) $\Lambda_e = \frac{1}{3}\Lambda_m$

(iv) $\Lambda_e = \frac{1}{6}\Lambda_m$

(b) $E°$ values of $Mg^{2+}|Mg$, $Zn^{2+}|Zn$ and $Fe^{2+}|Fe$ are –2·37 V, –0·76 V and –0·44 V respectively. Which of the following statements is correct?

(i) Mg^{2+} oxidises Fe

(ii) Zn oxidises Fe^{2+}

(iii) Zn reduces Mg^{2+}

(iv) Zn reduces Fe^{2+}

(c) The ionic mobility for alkali metal ions in aqueous solution is maximum for

(i) Na^+

(ii) K^+

(iii) Rb^+

(iv) Li^+

(d) The molecular dipole moment of chlorobenzene is 1·69 D. The dipole moments of *o*-, *m*- and *p*-dichlorobenzenes are

(i) 1·69 D, 2·93 D and 0 respectively

(ii) 0, 2·93 D and 1·69 D respectively

(iii) 2·93 D, 1·69 D and 0 respectively

(iv) 1·69 D, 2·69 D and 1·69 D respectively

2. Answer any *four* of the following questions : 2×4=8

(a) The standard reduction potential of $Cu^{2+}|Cu$ and $Cu^{2+}|Cu^+$ are 0·337 V and 0·153 V respectively. Calculate the standard electrode potential of $Cu^+|Cu$ half-cell.

(b) What is cell constant? How is it determined?

(c) Distinguish between an electrolytic cell and a galvanic cell.

(d) Why does the variation of equivalent conductivity on dilution of a strong electrolyte differ from that of a weak electrolyte?

(e) How do you account for the fact that the dipole moment of ethyl bromide (2·05 D) is considerably larger than that of chlorobenzene (1·70D)?

3. Answer any *two* of the following questions : 7×2=14

(a) (i) Explain clearly what is meant by Wien effect and Debye-Falkenhagen effect. 2+2=4

(ii) The specific conductance of a $0{\cdot}01$ mol dm^{-3} aqueous acetic acid solution at 298 K was $1{\cdot}65\times10^{-2}$ S m^{-1}. The equivalent conductance of acetic acid at infinite dilution was $390{\cdot}7\times10^{-4}$ S m^2 mol^{-1}. Calculate the degree of ionization (α) and the ionization constant (K_a) of the acid. 3

(b) (i) A decinormal solution of $AgNO_3$ was electrolyzed between platinum electrodes. After passing a small current for 2 hours, a fall of concentration of $5{\cdot}124\times10^{-4}$ gm equivalent occurred in the anodic solution. The mass of copper deposited in a copper coulometer placed in series was found to be $0{\cdot}0388$ gm. Calculate the transport number of silver and nitrate ions in silver nitrate ($AgNO_3$). (Equivalent mass of Cu = 31·8) 4

(ii) Discuss how the measurement of conductance can be applied to determine the solubility of a sparingly soluble salt. 3

(c) (i) Draw the curve showing the variation of conductance when acetic acid solution is titrated with sodium hydroxide solution and explain the reasons of such variation. 2+2=4

(ii) Derive the relation between ionic mobility and molar ionic conductance. 3

4. Answer any *two* of the following questions : 7×2=14

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

(ii) What is the potential of the cell containing two hydrogen electrodes as represented below? 3

$$Pt, H_2(g) \left| H^+ (10^{-8}\ M) \right\| H^+ (0{\cdot}001\ M) \left| H_2(g), Pt \right.$$

(iii) How will pH of aq. NaCl solution be effected when it is electrolyzed? 1

(b) (i) Cu does not dissolve in HCl but in HNO_3. Explain. 2

(ii) Which alkali metal is the most powerful reducing agent in aqueous solution and which halogen is the strongest oxidizing agent? 2

(iii) Discuss the cell construction and cell reactions of standard hydrogen electrode. State whether this electrode is reversible with respect to H_2 gas or H^+ ions. 2+1=3

(c) (i) The Gibbs' free energy for decomposition of Al_2O_3 at 500 °C is as follows :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$$

$$\Delta G = -966 \text{ kJ mol}^{-1}$$

Calculate the potential difference needed for electrolytic reduction of Al_2O_3. 3

(ii) What are concentration cells? Derive an expression for the e.m.f. of a concentration cell without transference. 3

(iii) What do you mean by standard electrode potential? 1

(d) (i) Metal rod *A* is dipped in 0·1 *M* solution of AsO_4. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. Given $E^\circ_{A^{2+}|A} = -0{\cdot}76$ V. 3

(ii) Calculate K_c for the cell reaction

$$4Br^- + O_2 + 4H^+ \rightarrow 2Br_2 + 2H_2O;$$

$$E^\circ_{cell} = 0{\cdot}16 \text{ V}$$ 2

(iii) "Daniell cell is a reversible cell." Justify the statement. 2

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

(a) (i) Define any *two* of the following : 1×2=2

(1) Electronic polarization

(2) Atomic polarization

(3) Orientation polarization

(ii) Stating all the terms involved, write the suitable form of Clausius-Mossotti equation. Explain why this equation is applicable for non-polar molecules and not for polar molecules. 1½+1½=3

(b) Define paramagnetic and diamagnetic substances on the basis of their values of magnetic susceptibility and intensity of magnetization. The dipole moment of HCl molecule is 1·03D and it is 17% ionic. Find its bond distance. 2+3=5

$$\left[\begin{array}{l} e = 1{\cdot}60 \times 10^{-19} c \\ \quad = 4{\cdot}8 \times 10^{-10} \text{ esu} \end{array}\right]$$

(c) What is magnetic susceptibility? What is the relation between magnetic susceptibility and magnetic moment? Explain. What is the SI unit of magnetic susceptibility? 2+2+1=5

6. Answer any *one* of the following questions : 3

(a) Discuss Gouy's method for determination of magnetic susceptibility of a substance.

(b) The dielectric constant of nitrogen at NTP is 1·004 and also its density is 1·25 gm/litre. Calculate the induced molar polarization and polarizability of the molecule.

(c) Calculate the liquid junction potential associated with the following cell at 25 °C :

$$Ag\,(s),\ AgCl\,(s),\ HCl\ (m_1 = 1{\cdot}0,\ \gamma_1 = 0{\cdot}809)\,||\,HCl\ (m_2 = 0{\cdot}05,\ \gamma_2 = 0{\cdot}830),\ AgCl\,(s),\ Ag\,(s)$$

If the transference number of H^+ is 0·83.

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