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(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 $\text{Al}_2(\text{SO}_4)_3$ is

(i) $\Lambda_e = \Lambda_m$

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

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

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

(2)

(b) E° values of $\text{Mg}^{2+}|\text{Mg}$, $\text{Zn}^{2+}|\text{Zn}$ and $\text{Fe}^{2+}|\text{Fe}$ 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

(3)

2. Answer any *four* of the following questions :

$2 \times 4 = 8$

(a) The standard reduction potential of $\text{Cu}^{2+}|\text{Cu}$ and $\text{Cu}^{2+}|\text{Cu}^+$ are 0.337 V and 0.153 V respectively. Calculate the standard electrode potential of $\text{Cu}^+|\text{Cu}$ 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 (1.70 D)?

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

$7 \times 2 = 14$

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

$2 + 2 = 4$

(4)

(ii) The specific conductance of a 0.01 mol dm^{-3} aqueous acetic acid solution at 298 K was $1.65 \times 10^{-2} \text{ S m}^{-1}$. The equivalent conductance of acetic acid at infinite dilution was $390.7 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$. 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 $5.124 \times 10^{-4} \text{ gm}$ equivalent occurred in the anodic solution. The mass of copper deposited in a copper coulometer placed in series was found to be 0.0388 gm . Calculate the transport number of silver and nitrate ions in silver nitrate (AgNO_3). (Equivalent mass of $\text{Cu} = 31.8$)

4

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

3

(5)

(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 :

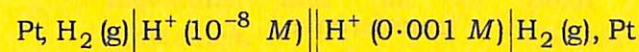
7×2=14

(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



(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

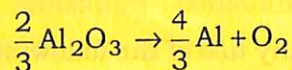
(ii) Which alkali metal is the most powerful reducing agent in aqueous solution and which halogen is the strongest oxidizing agent?

2

(6)

(iii) Discuss the cell construction and cell reactions of standard hydrogen electrode. State whether this electrode is reversible with respect to H₂ gas or H⁺ ions. 2+1=3

(c) (i) The Gibbs' free energy for decomposition of Al₂O₃ at 500 °C is as follows :



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

Calculate the potential difference needed for electrolytic reduction of Al₂O₃. 3

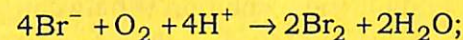
(ii) What are concentration cells? Derive an expression for the e.m.f. of a concentration cell without transference. 3

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

(d) (i) Metal rod A is dipped in 0.1 M solution of AsO₄. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. Given $E_{A^{2+}|A}^\circ = -0.76 \text{ V}$. 3

(7)

(ii) Calculate K_c for the cell reaction



$$E_{\text{cell}}^\circ = 0.16 \text{ V} \quad 2$$

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

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

$$5 \times 2 = 10$$

(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

$$\left[\begin{array}{l} e = 1.60 \times 10^{-19} \text{ c} \\ = 4.8 \times 10^{-10} \text{ esu} \end{array} \right]$$

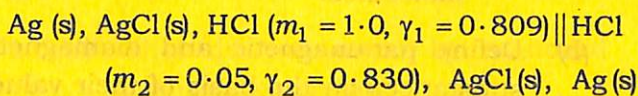
- (c) What is magnetic susceptibility? What is the relation between magnetic susceptibility and magnetic moment? Explain. What is the SI unit of magnetic susceptibility? 2+2+1=5

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 :



If the transference number of H^+ is 0.83.

★ ★ ★