3 (Sem–4/CBCS) CHE HC 3

2024

CHEMISTRY

(Honours Core)

Paper : CHE–HC–4036

(Physical Chemistry–IV)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions : $1 \times 7 = 7$

(a) The molar conductance Λ°_{NaOAC} and Λ°_{HCl} at infinite dilution in water at $25^{\circ}C$ are $91 \cdot 0$ and $426 \cdot 2$ $S\,cm^2\,mol^{-1}$ respectively. To calculate Λ°_{HOAC}, the additional value required is

(i) Λ°_{NaOH}

(ii) Λ°_{NaCl}

(iii) $\Lambda^{\circ}_{H_2O}$

(iv) Λ°_{KCl}

(Choose the correct answer)

Contd.

(b) Define specific conductance.

(c) What is Ostwald's Dilution Law ?

(d) The pH of an aqueous solution is 4. Its $\left[OH^-\right]$ is

    (i)   10

    (ii) 10^{-4}

    (iii) 10^{-10}

    (iv) 10^{-14}

               (Choose the correct answer)

(e) Define Debye-Falkenhagen effect.

(f) Which of the following molecule would have zero dipole moment ?

    (i) NH_3

    (ii) m-dichlorobenzene

    (iii) CH_3Cl

    (iv) p-dichlorobenzene

               (Choose the correct answer)

(g) The relative permeability $\mu_r > 1$ stands for

    (i)   Paramagnetic solids

    (ii) Diamagnetic solids

    (iii) Ferromagnetic solids

    (iv) None of the above

               (Choose the correct answer)

2. Answer the following questions :   2×4=8

(a) Explain the variation of molar conductance with dilution for weak electrolyte.

(b) Name *two* types of concentration cells.

(c) How can dissociation constant of weak acid be determined from the measurement of conductance ?

(d) Differentiate between paramagnetic and diamagnetic substances in terms of magnetic permeability and magnetic susceptibility.

3. Answer *any three* questions from the following :   5×3=15

(a) What is meant by transport number of an ion ? How is it determined by moving boundary method ?   1+4=5

(b) Explain saturated calomel electrode with the reactions when it is acting as anode and cathode as well.

(c) At 25 °C, the specific conductance of carefully distilled water is $58 \cdot 0 \times 10^{-7}$ Sm^{-1} and λ_m° values for H^+ and OH^- ions are $349 \cdot 8 \times 10^{-4}$ and $198 \cdot 5 \times 10^{-4}$ $Sm^2\,mol^{-1}$ respectively. Calculate the ionic product of water at 25°C. [Assume that λ_m differs very little from λ_m°]

(d) Derive the relation between standard EMF and equilibrium constant of a cell reaction. The standard EMF of the cell

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

is $1 \cdot 10$ volts. Calculate the equilibrium constant of the cell reaction. Prove whether the reaction is feasible or not.

2+2+1=5

(e) What is magnetic susceptibility ? Explain Gouy's method for the measurement of magnetic susceptibility. 1+4=5

4. Answer *any three* questions from the following : 10×3=30

(a) Discuss Debye-Hückel theory of strong electrolytes. Explain relaxation effect and electrophoretic effect. How can Debye-Hückel-Onsager equation be utilized in the determination of equivalent conductance at infinite dilution for stong electrolytes.

3+4+3=10

(b) Write the principle of conductometric titrations. Draw and explain the titration curves obtained in the conductometric titration of

(i) HCl with $NaOH$

(ii) CH_3COOH with $NaOH$

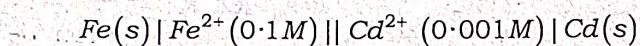(iii) CH_3COOH with NH_4OH and

(iv) $AgNO_3$ with KCl

2+2+2+2+2=10

(c) Explain the construction and working of glass electrode for the determination of pH of a solution using this electrode. What are the limitations of a glass electrode ? 8+2=10

(d) Derive Nernst equation for the measurement of EMF of an electro-chemical cell.

Consider an electrochemical cell

$$Fe(s)\,|\,Fe^{2+}(0\cdot1M)\,||\,Cd^{2+}(0\cdot001M)\,|\,Cd(s)$$

(i) Write the cell reaction

(ii) Calculate the EMF of the cell

(iii) Calculate $\Delta G°$ value of the cell reaction.

Given that $E°_{Cd^{2+}|Cd} = -0\cdot40V$

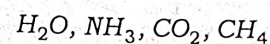$$E°_{Fe^{2+}|Fe} = -0\cdot44V$$

why does a cell stops working after some time ? Explain with an example.

$$3+1+2+2+2=10$$

(e) (i) What is molecular polarizability ?

(ii) Derive the Clausius-Mossotti equation.

(iii) Define induced molar polarization.

(iv) Which of the following molecules obey Clausius-Mossotti equation ? H_2O, NH_3, CO_2, CH_4

$$2+5+1+2=10$$

(f) (i) How can you apply dipole moment of a molecule to calculate percentage ionic character of the molecule and to predict the shapes of molecules ?

(ii) The dipole moment of $NH_3(g)$ is 1·46D and the bond angle HNH is 108°. Calculate the bond moment of the $N-H$ bond.

(iii) How do you explain that the dipole moment of ethylchloride is considerably larger than that of chlorobenzene ?

$$6+2+2=10$$

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