Total number of printed pages–11

3 (Sem–4/CBCS) CHE HC 3

2025

CHEMISTRY

(Honours)

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 ***any seven*** of the following questions : 1×7=7

   (a) Define specific conductance of an electrolyte.

   (b) Under what conditions will a galvanic cell send no current in the outer circuit ?

   (c) What is the charge in coulombs on CO_3^{2-} ion ?

   (d) Define Wien effect.

(e) What is the relationship between molar conductivity and equivalent conductivity of an electrolyte A_xB_y ?

(f) The conductivity of $N/10KCl$ solution at $20°C$ is $0.0212\ S\ cm^{-1}$ and the resistance of the cell containing this solution is 55 ohms. The cell constant in cm^{-1} is

(i) 4.6

(ii) 0.616

(iii) 2.17

(iv) 1.166

(Choose the correct option)

(g) Define magnetic susceptibility.

(h) Which of the following molecules would have zero dipole moment ?

(i) *m*-dichlorobenzene

(ii) *p*-dichlorobenzene

(iii) CH_3Cl

(iv) NH_3

(Choose the correct option)

(i) What is magnetic permeability ?

(j) Fluorine cannot be prepared from fluorides by chemical oxidation. Why ?

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

(a) Explain why mobility of H^+ ion is highest in aqueous solution.

(b) Write the reaction that takes place in *Ag–AgCl* electrode. Also write Nernst equation for the same.

(c) The molar conductances at infinite dilution of $NaOH$, $NaCl$ and $BaCl_2$ are $2.481\times10^{-2}Sm^2mol^{-1}$, $1.265\times10^{-2}Sm^2mol^{-1}$ and $2.80\times10^{-2}Sm^2mol^{-1}$ respectively. Calculate molar conductance at infinite dilution of $Ba(OH)_2$.

(d) Given, $E^oCu^{2+}\,|\,Cu = 0.34V$ and $E^oAl^{3+}\,|\,Al = -1.66V$. Calculate the equilibrium constant of the following reaction at $298\ K$:

$$2Al(s) + 3CuSO_4(aq) \rightleftharpoons Al_2(SO_4)_3(aq) + 3Cu(s)$$

(e) Explain why mobility of Li^+ is less than that of K^+ ion aqueous medium.

(f) Explain the terms 'induced polarization' and 'orientation polarization'.

(g) What is dipole moment ? What are its units ?

(h) The dipole moment of $NH_3(g)$ is 1.46D. If the angle HNH is 108°, calculate the bond moment of N–H bond.

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

(a) Using Debye-Huckel theory discuss about different factors that affect the speed of ion when an electric field is applied.

(b) Deduce an expression for the e.m.f. of the concentration cell with transference :

$$Pt(s)\,|\,H_2(1atm)\,|\,HCl(a_1):HCl(a_2)\,|\,H_2(1atm)\,|\,Pt(s)$$

(c) (i) Explain the moving boundary method for determination of transport number of ions. 3

(ii) Write the electrode reaction of calomel electrode when the cell acts as cathode. Give the expression for potential of a calomel electrode. 2

(d) (i) Calculate the mean ionic activity coefficient of 0.01 M Na_2SO_4 solution in water at 298 K. 3

(ii) Calculate the standard free energy change associated with the reaction : 2

$$2Al(s)+3ZnSO_4(aq)\rightarrow Al_2(SO_4)_3(aq)+3Zn(s)$$

Given :

$$E^o_{Al^{3+}|Al}=-1.66V \text{ and}$$

$$E^o_{Zn^{2+}|Zn}=-0.76V$$

(e) What is meant by polarizability of a molecule ? Derive the Clausius–Mossotti equation. 1+4=5

(f) What information regarding the structure of molecules can be obtained from the knowledge of their dipole moments ? What are meant by bond moment and group moment ? 3+2=5

(g) Give a brief account of Lorentz-Lorentz equation.

(h) Calculate the solubility product of the sparingly soluble salt CaF_2 from the following data :

The molar ionic conductances (at infinite dilution) of Ca^{2+} and F^- ions are 104×10^{-4} and $48\times10^{-4}\ Sm^2\ mol^{-1}$ respectively. The specific conductance of the saturated solution of CaF_2 at room temperature is $4.25\times10^{-3}\ Sm^{-1}$ and the specific conductance of water used for preparing the solution is $2\times10^{-4}\ Sm^{-1}$.

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

(a) (i) A solution of HCl was electrolysed in a Hittorf cell using Pt electrodes. The analysis of the solution from the cathode compartment before and after electrolysis indicated the masses of HCl as $1.82\times10^{-4}\ kg$ and $1.67\times10^{-4}\ kg$ respectively. At

the same time the mass of Ag deposited at the cathode of the coulometer in the same circuit was found to be $2.52\times10^{-4}\ kg$. Calculate the transport number of each ion. 4

(ii) Write what you mean by concentration cell. Taking the example of hydrogen electrode, explain how concentration cells are classified. Explain in which type of cell liquid junction potential will be maximum. 1+3+2=6

(b) What is the principle underlying conductometric titrations ? Discuss the titration curves obtained in the titration of :

(i) a strong acid with a strong base;

(ii) a strong acid with a weak base;

(iii) a mixture of HCl and CH_3COOH with $NaOH$;

(iv) $AgNO_3$ against KCl.

2+2+2+2+2=10

(c) (i) Write Nernst equations for the potentials of *Zn*-electrode and *Cu*-electrode in the Daniell cell. Hence find an expression for the e.m.f. of the Daniell cell at any given temperature. 2+2=4

(ii) For the reaction $Fe^{3+} + 3e^- \rightleftharpoons Fe$, standard electrode potential is $-0.036\ V$ and the standard electrode potential for the reaction $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ is $0.771\ V$. Calculate the standard electrode potential for the reaction $Fe^{2+} + 2e^- \rightleftharpoons Fe$. Predict whether the reaction $Fe + 2Fe^{3+} \rightleftharpoons 3Fe^{2+}$ is spontaneous or not. 4+2=6

(d) (i) Deduce the relationship between ion mobility and molar conductance of an electrolyte. 4

(ii) What do you mean by activity coefficient ? Taking an example, discuss how mean ionic activity coefficient can be found out from e.m.f. measurement. 1+3=4

(iii) Calculate the EMF of the following electrode concentration cell at $298K$: 2

$$Pb(Hg)(a_1 = 0.2) \mid Pb(NO_3)_2(aq) \mid Pb \mid Hg(a_2 = 0.02)$$

(e) (i) Discuss the principle underlying potentiometric titrations. Discuss the variation of potential with volume of *NaOH* added in the titration against *HCl* ? In what respect potentiometric titrations are better than simple volumetric titrations ? 2+2+2=6

(ii) Explain a method of measurement of magnetic susceptibility of a substance. 4

(f) (i) Explain how the dipole moment of a gaseous molecule can be determined by using the Debye equation. 6

(ii) Estimate the refractive index of water, given that the polarizability volume of water molecule at optical frequencies is $1.5 \times 10^{-24} cm^3$. 4

(g) (i) Conductivity of a 0.02 *mol ohm*$^{-3}$ solution of acetic acid at 298*K* is $2.324\times10^{-2} Sm^{-1}$. If the molar conductance of the acetic acid solution of infinite dilution is $387.9\times10^{-4} Smol^{-1}m^2$, calculate the degree of dissociation of acetic acid in the solution at 298*K*. 3

(ii) The molar ionic conductance at infinite dilution of silver ions is $61.92\times10^{-4} Sm^2 mol^{-1}$ at 25°*C*. Calculate the ionic mobility of silver ions at 25°*C* at infinite dilution. 3

(iii) In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold salt and second cell contains copper sulphate solution. 9.85*g* of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere. 4

(h) (i) What are meant by electronic polarisation and atomic polarisation ? 2

(ii) What is drift velocity of ions in solution ? What is abnormal transference number ? Give *one* example. 2+3=5

(iii) The standard electrode potentials of Pb/Pb^{2+} and $Pt/I^-/I_2$ are −0.126 volt and + 0.536 volt respectively. When a galvanic cell is constructed using 0.1 molar concentrations of the respective ions, *Pt* is found to be the cathode. What is the voltage generated in the cell ? 3