**TDC (CBCS) Even Semester Exam., 2023**

# CHEMISTRY

## ( Honours )

**( 4th Semester )**

Course No. : CHMHCC–403T

**( Physical Chemistry—IV )**

*Full Marks* : 50
*Pass Marks* : 20

*Time* : 3 hours

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

## SECTION—A

Answer any *ten* of the following questions : 2×10=20

**1.** Choose the correct answer :

*(a)* The increase in equivalent conductance of a strong electrolyte with dilution is due to

*(i)* increase in number of ions

*(ii)* increase in ionic mobility of ions

(iii) 100% ionization of electrolyte at normal dilution

(iv) increase in number of ions and ionic mobility of ions

(b) For strong electrolytes $\Lambda_m^c$ increases with dilution because ____ attraction decreases but for weak electrolytes $\Lambda_m^c$ increases with dilution because ____ increases.

(i) interionic, dissociation

(ii) intraionic, dissociation

(iii) All of the above

(iv) None of the above

2. With the help of graph, explain why it is not possible to determine the molar conductivity at infinite dilution for a weak electrolyte by extrapolating the concentration–molar concentration curve.

3. State and explain Kohlrausch law of independent migration of ions with a suitable example.

4. Discuss the factors affecting transport number.

5. Define transference number with respect to cation and anion.





6. Derive the expression for mobility of an ion.

7. Explain the formation of products of electrolysis of aqueous $CuSO_4$ solution using platinum electrodes showing primary and secondary changes.

8. Derive the Nernst equation for a general reaction of the type $aA + bB \rightleftharpoons cC + dD$.

9. Write the electrode reaction, net reaction and the cell notation for an electrode reversible with respect to anion.

10. Write the relation and explain the terms for (a) free energy change with e.m.f. and (b) enthalpy change with e.m.f.

11. What is liquid junction potential? Explain its significance.

12. Explain the principle of potentiometric titration with reference to acid-base reaction.

13. Explain diamagnetism.

14. What is dielectric electrostatics?

15. Define paramagnetism with example.

SECTION—B

Answer any *five* of the following questions : 6×5=30

16. (a) Derive the relation between equivalent conductivity and specific conductivity of an electrolyte solution. 2

(b) Explain Arrhenius theory of electrolytic dissociation. 1½

(c) The molar conductivities at infinite dilution for barium hydroxide, barium chloride and ammonium chloride are 457·6, 240·6 and 129·8 $ohm^{-1}cm^2mol^{-1}$ respectively. Calculate the molar conductivity at infinite dilution for ammonium hydroxide. 2½

17. (a) Write the Debye-Hückel-Onsager equation and explain the terms involved. 1½

(b) Explain the following terms : 2

(i) Relaxation effect

(ii) Electrophoretic effect

(c) The conductivity of a solution containing 1 g of anhydrous barium chloride in 200 $cm^3$ of water has been found to be 0·0058 S $cm^{-1}$. What are the molar conductivity and equivalent conductivity of the solution (atomic weight Ba–137, Cl–35·5)? 2½





18. (a) Explain the determination of transference using moving boundary method. 2½

(b) Discuss the application of conductance measurement in conductometric titration with a suitable example. 1½

(c) The specific conductances of a sparingly soluble salt (1 : 1) (200 g $mol^{-1}$) in its saturated aqueous solution at 25 °C and that of water are $1·5 \times 10^{-3}$ and $1·5 \times 10^{-5}$ ohm $dm^{-1}$, and ionic conductances for cation and anion are 0·485 and 1·0 $ohm^{-1}$ $dm^2$ $mol^{-1}$. Find the solubility of salt in g $L^{-1}$. 2

19. (a) Explain how transference number can be determined by using Hittorf's method. 2½

(b) A solution of $AgNO_3$ was electrolyzed between Ag electrodes. Before electrolysis, 10 g of the solution contained 0·01788 g of $AgNO_3$. After the experiment, 20·09 g of the anodic solution contained 0·06227 g $AgNO_3$. At the same time, 0·009479 g of Cu was deposited in Cu coulometer placed in series. Calculate the transport number of $Ag^+$ and $NO_3^-$ ions. (Ag = 108, Cu = 63·6). 3½

**20.** *(a)* Write the electrode reaction and cell notation for an electrode which consists of metal, one of its insoluble salts, another insoluble salt of another metal having same anion and the solution of any soluble salt having the common cation to the latter salt. 1½

*(b)* A current of 4 amp was passed for 1·5 hours through a solution of $CuSO_4$ and 3·2 g of Cu was deposited. Calculate the current efficiency. 2½

*(c)* Describe the construction of a calomel electrode with a suitable diagram, the half reaction and cell notation. 2

**21.** *(a)* Explain the electrolytic extraction of aluminium from alumina by Hall and Heroult's process. 2½

*(b)* Explain reversible cell with a suitable example. 1

*(c)* Two electrolytic cells containing $AgNO_3$ solution and dil. $H_2SO_4$ solution were connected in series. A current of 2·5 amp was passed through them





till 1·078 g of Ag was deposited (Ag—107·8 g $mol^{-1}$).

*(i)* How much of electricity was consumed?

*(ii)* What was the weight of $O_2$ gas liberated? 2½

**22.** *(a)* Derive the following relation : 1½

$$\Delta S = n\left(\frac{\partial E}{\partial T}\right)_P$$

*(b)* Derive the expression for EMF of an electrolytic concentration cell without transference which is reversible with respect to cation. 2

*(c)* Calculate the equilibrium constant for the reaction $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$.

Given

$E^\circ_{Zn^{2+}/Zn} = -0 \cdot 76$ V; $E^\circ_{Cu^{2+}/Cu} = 0 \cdot 34$ V 2½

**23.** *(a)* Derive an expression using EMF to determine the pH of an unknown solution by using a hydrogen electrode. 2½

*(b)* Derive the EMF expression for a concentration cell with transport taking a suitable example. 3½

**24.** *(a)* Deduce Clausius-Mösotti equation. 3

*(b)* Explain the following terms : 3

*(i)* Induced polarization

*(ii)* Orientation polarization

**25.** *(a)* Derive Lorentz-Lorenz equation. 2

*(b)* Explain how dipole moment can be measured using temperature method. 2

*(c)* What is magnetic susceptibility and how can it be measured? 2

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