

Total No. of Printed Pages—11

4 SEM TDC CHM M 1 (N/O)

2020

CHEMISTRY

(Major)

Course : 401

(Physical Chemistry)

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

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Choose the correct answer from the following : 1×5=5

(a) A current of 0.1 A is passed through an aqueous solution of copper sulphate for 15 minutes using platinum electrode. The amount of copper deposited at the cathode is

- (i) 0.02963 g
- (ii) 2.808×10^{20} g
- (iii) 0.05703 g
- (iv) 0.6375 g

- (b) At 300 K, the value of $\Delta G - \Delta A$ is zero for the reaction
- (i) $\text{H}_2\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$
 - (ii) $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) = \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$
 - (iii) $\text{PCl}_5(\text{g}) = \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - (iv) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$
- (c) The observed conductance is maximum for
- (i) 0.1 M KCl solution
 - (ii) 0.1 M NaOH solution
 - (iii) 0.1 M HCl solution
 - (iv) 0.1 M CH_3COOH solution
- (d) Electrode potential of a standard hydrogen electrode is
- (i) 1.0 V
 - (ii) 0 V
 - (iii) -1.0 V
 - (iv) 0.5 V
- (e) The correct order of mobility of the alkali metal ions in aqueous solution is
- (i) $\text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Li}^+$
 - (ii) $\text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
 - (iii) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$
 - (iv) $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+$

2. Answer any *five* questions from the following : 2×5=10

- (a) Show that for a reversible phase transformation, Gibbs' free energy change is zero.
- (b) Distinguish a reversible cell from an irreversible cell.
- (c) Why does the variation of equivalent conductivity on dilution of a strong electrolyte differ from that of a weak electrolyte?
- (d) Describe standard hydrogen electrode.
- (e) Explain the physical significance of Gibbs' free energy and Helmholtz free energy.
- (f) Calculate the entropy change for the fusion of 1 mole of ice at 0 °C. Given $\Delta H_{\text{fus(ice)}} = 334.72 \text{ J g}^{-1}$.

3. Answer any *two* questions from the following : 4½×2=9

- (a) Deduce an expression for the entropy changes associated with the changes in temperature and pressure of an ideal gas. 4½

(b) (i) Prove that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 2\frac{1}{2}$$

(ii) State and explain Nernst's heat theorem. 2

(c) (i) State and explain the third law of thermodynamics. 1½

(ii) Calculate the entropy change accompanying the freezing of one mole of water at 25 °C to ice at -10 °C, given that the heat of fusion of ice at its fusion point (0 °C) is 6.00 kJ mol⁻¹, the heat capacity of ice is 36.82 JK⁻¹ and heat capacity of liquid water is 75.31 JK⁻¹ mol⁻¹. 3

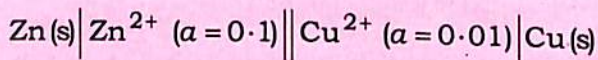
4. Answer any *two* questions from the following : 7×2=14

(a) (i) Represent the variation of equivalent conductance of KCl and CH₃COOH with dilution graphically and give explanation for such variation. 4

(ii) What are ionic mobilities? Derive a relation between ionic mobility and molar ionic conductance. 1+2=3

- (b) (i) State and explain Kohlrausch's law of independent migration of ions. 3
- (ii) The ionic conductivities of Li^+ and Na^+ ions are $38.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and $50.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. Calculate their mobilities. 3
- (iii) What is Wien effect? 1
- (c) (i) Explain how the degree of hydrolysis and hydrolysis constant of aniline hydrochloride can be determined from conductance measurement. 4
- (ii) Sketch schematically the conductometric titration curve for a strong base by a weak acid and describe it. $1+2=3$
5. Answer any two questions from the following : $5 \times 2 = 10$
- (a) Derive an expression for the e.m.f. of a concentration cell with transference. 5
- (b) (i) With the help of mathematical expression, explain how the cell e.m.f. is used in calculating ΔG , ΔH and ΔS for a cell reaction. 3

- (ii) Draw a schematic diagram of H_2-O_2 fuel cell. 2
- (c) (i) Derive an equation showing the effect of electrolyte concentration on electrode potential. 3
- (ii) Calculate the potential of the following cell at 298 K : 2



Given, $E_{Zn^{2+}/Zn}^{\circ} = -0.762 \text{ V}$

$E_{Cu^{2+}/Cu}^{\circ} = +0.337 \text{ V}$

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Choose the correct answer from the following : 1×5=5

(a) Li^+ has a smaller ionic mobility than K^+ because of the

- (i) larger size of Li^+
- (ii) larger radius to charge ratio of Li^+
- (iii) greater degree of hydration of Li^+
- (iv) smaller nuclear charge of Li^+

(b) When one faraday of electricity is passed through CuSO_4 solution, number of atoms formed at cathode will be

- (i) 6.02×10^{23}
- (ii) 3.01×10^{23}
- (iii) 2
- (iv) 6.02×10^{-23}

(c) For a standard hydrogen electrode, the electrode potential is

- (i) 1.0 V
- (ii) 0 V
- (iii) -1.0 V
- (iv) 0.5 V

- (d) The equilibrium which is not affected by pressure changes is
- (i) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - (ii) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 - (iii) $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$
 - (iv) $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
- (e) Standard electrode potentials of three metals X, Y and Z are -1.2 V , $+0.5\text{ V}$ and -3.0 V respectively. The reducing power of three metals will be
- (i) $Z > X > Y$
 - (ii) $X > Y > Z$
 - (iii) $Y > Z > X$
 - (iv) $Y > X > Z$

2. Answer the following questions : 2×5=10

- (a) Define chemical potential. What is its physical significance?
- (b) Why does the variation of equivalent conductivity on dilution of a strong electrolyte differ from that of a weak electrolyte?
- (c) Describe standard hydrogen electrode.
- (d) Distinguish a reversible cell from an irreversible cell.
- (e) What is liquid junction potential?

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

(a) (i) Represent the variation of equivalent conductance of KCl and CH₃COOH with dilution graphically and give explanation for such variation. 4

(ii) What are ionic mobilities? Deduce a relation between ionic mobility and molar ionic conductance. 1+2=3

(b) (i) State and explain Kohlrausch's law of independent migration of ions. 3

(ii) Calculate the equivalent and molar conductances of aqueous BaSO₄ solution at infinite dilution. Given

$$\Lambda_{\frac{1}{2}\text{Ba}(\text{NO}_3)_2}^{\circ} = 135.04 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ equiv}^{-1}$$

$$\Lambda_{\frac{1}{2}\text{H}_2\text{SO}_4}^{\circ} = 429.60 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ equiv}^{-1}$$

$$\Lambda_{\text{HNO}_3}^{\circ} = 421.24 \times 10^{-4} \Omega^{-1} \text{ m}^2 \text{ equiv}^{-1} \quad 4$$

(c) (i) Explain how the degree of hydrolysis and hydrolytic constant of aniline hydrochloride can be determined from conductance measurement. 4

- (ii) Sketch schematically the conductometric titration curve for a strong acid by a strong base and describe it. 1+2=3

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

- (a) (i) Derive an expression for the e.m.f. of a concentration cell with transference. 4

- (ii) Write any one difference between galvanic cell and electrolytic cell. 1

- (b) What is glass electrode? Describe how the pH of a solution can be measured with the help of glass electrode. 1+4=5

- (c) (i) Show that the e.m.f. of a cell can be used to calculate the equilibrium constant of a cell reaction. 3

- (ii) Give a brief description of lead storage cell. 2

5. Answer any *three* questions from the following : 3×3=9

- (a) Discuss the effect of temperature and pressure of chemical potential. 3

- (b) Establish the relationship between ΔG° and K_c of a reversible reaction. 3

- (c) Derive Gibbs-Duhem equation for two-component system. 3
- (d) (i) What is fugacity? Write its physical significance. 1+1=2
- (ii) Write the effect of pressure on the following equilibrium : 1

