

Total No. of Printed Pages—12

4 SEM TDC CHM M 1 (N/O)

2017

(May)

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. Select the correct answer : 1×5=5

(a) The solution of KCl which has the lowest value of equivalent conductance is

(i) 1 M

(ii) 0.1 M

(iii) 0.01 M

(iv) 0.001 M

(b) At infinite dilution, the equivalent conductances of CH_3COONa , HCl and CH_3COOH are $91 \text{ mho cm}^2 \text{ eq}^{-1}$, $426 \text{ mho cm}^2 \text{ eq}^{-1}$ and $391 \text{ mho cm}^2 \text{ eq}^{-1}$ respectively at 25°C . The equivalent conductance of NaCl at infinite dilution is

(i) $126 \text{ mho cm}^2 \text{ eq}^{-1}$

(ii) $209 \text{ mho cm}^2 \text{ eq}^{-1}$

(iii) $391 \text{ mho cm}^2 \text{ eq}^{-1}$

(iv) $908 \text{ mho cm}^2 \text{ eq}^{-1}$

(c) In a galvanic cell

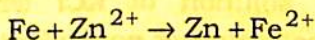
(i) chemical reaction produces electrical energy

(ii) electrical energy produces chemical reaction

(iii) reduction occurs at anode

(iv) oxidation occurs at cathode

(d) E° for the reaction



is -0.35 V . The given cell reaction is

(i) feasible

(ii) not feasible

(iii) in equilibrium

(iv) not predictable

(e) The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is $75 \text{ J mol}^{-1} \text{ K}^{-1}$. The boiling point of the liquid at one atmosphere is

(i) 250 K

(ii) 400 K

(iii) 450 K

(iv) 600 K

2. Answer any five of the following questions :

2×5=10

(a) Molar conductance at infinite dilution of weak electrolytes cannot be determined by graphical methods. Explain why.

(b) Describe standard hydrogen electrode.

(c) State and explain Walden's rule.

(d) Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

(e) Describe how work function varies with temperature at constant volume.

(f) The enthalpy and entropy change for a chemical reaction are $-2.5 \times 10^3 \text{ cal}$ and 7.4 cal deg^{-1} respectively. Determine whether the reaction is spontaneous or not at 298 K.

UNIT—I

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

$4\frac{1}{2} \times 2 = 9$

(a) Deduce an expression for efficiency of a Carnot engine working between two temperatures T_1 and T_2 . 4½

(b) (i) Explain how the third law of thermodynamics can be used for the evaluation of absolute entropy of a substance. 2½

(ii) Calculate the change in Gibbs' free energy accompanying the compression of 1 mole of CO_2 at 57°C from 5 atm to 50 atm. Assume that CO_2 behaves like an ideal gas. 2

(c) (i) Prove that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
2½

(ii) Write the physical significance of Helmholtz free energy and Gibbs' free energy. 2

UNIT—II

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

7×2=14

(a) (i) What are ionic mobilities? Derive a relation between ionic mobility and molar ionic conductance. 1+3=4

(ii) What is abnormal transport number of an ion? Under what condition, an aqueous solution of CdI_2 shows the negative transport number of Cd^{2+} ion? 1+2=3

(b) Define specific, molar and equivalent conductances. Explain why specific conductance decreases with dilution but the molar conductance increases. 3+4=7

(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 curves for a strong acid by a strong base and a strong acid by a weak base. $1\frac{1}{2}+1\frac{1}{2}=3$

UNIT—III

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

5×2=10

(a) (i) Give one example each of electrode concentration cell and electrolyte concentration cell. 2

(ii) Describe how the pH of a solution can be measured with the help of a hydrogen electrode. 3

(b) (i) Derive an equation showing the effect of electrolyte concentration on electrode potential. 4

(ii) Give one example of fuel cell. 1

(c) The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 V and 0.799 V respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of Ag^+ will the e.m.f. of the cell at 25 °C be zero if the concentration of Cu^{2+} is 0.01 M?

2+3=5

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Select the correct answers : 1×5=5

(a) The solution of KCl which has the lowest value of equivalent conductance is

(i) 1 M

(ii) 0.1 M

(iii) 0.01 M

(iv) 0.001 M

(b) At infinite dilution, the equivalent conductances of CH_3COONa , HCl and CH_3COOH are $91 \text{ mho cm}^2 \text{ eq}^{-1}$, $426 \text{ mho cm}^2 \text{ eq}^{-1}$ and $391 \text{ mho cm}^2 \text{ eq}^{-1}$ respectively at 25°C . The equivalent conductance of NaCl at infinite dilution is

(i) $126 \text{ mho cm}^2 \text{ eq}^{-1}$

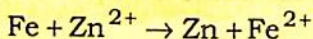
(ii) $209 \text{ mho cm}^2 \text{ eq}^{-1}$

(iii) $391 \text{ mho cm}^2 \text{ eq}^{-1}$

(iv) $908 \text{ mho cm}^2 \text{ eq}^{-1}$

- (c) In a galvanic cell
- (i) chemical reaction produces electrical energy
 - (ii) electrical energy produces chemical reaction
 - (iii) reduction occurs at anode
 - (iv) oxidation occurs at cathode

- (d) E° for the reaction



is -0.35 V. The given cell reaction is

- (i) feasible
 - (ii) not feasible
 - (iii) in equilibrium
 - (iv) not predictable
- (e) The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if
- (i) temperature is increased and pressure is kept constant
 - (ii) temperature is reduced and pressure is increased
 - (iii) both temperature and pressure are increased
 - (iv) both temperature and pressure are reduced

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

2×5=10

- (a) Molar conductance at infinite dilution of weak electrolytes cannot be determined by graphical methods. Explain why.
- (b) Describe standard hydrogen electrode.
- (c) State and explain Walden's rule.
- (d) Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.
- (e) Write the effect of temperature and pressure on chemical potential.
- (f) Explain the term 'partial molar quantities'.
- (g) Use of NH_4NO_3 in agar bridge minimizes the liquid junction potential. Explain.

UNIT—I

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

7×2=14

- (a) (i) What are ionic mobilities? Derive a relation between ionic mobility and molar ionic conductance. 1+3=4

(ii) What is abnormal transport number of an ion? Under what condition, an aqueous solution of CaI_2 shows the negative transport number of Cd^{2+} ion? 1+2=3

(b) (i) Define specific, molar and equivalent conductances. Explain why specific conductance decreases with dilution but the molar conductance increases. 3+2=5

(ii) The conductivity of 0.20 M KCl solution at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity. 2

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

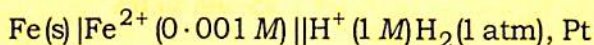
(ii) Sketch schematically the conductometric titration curves for a strong acid by a strong base and a strong acid by a weak base. $1\frac{1}{2}+1\frac{1}{2}=3$

UNIT—II

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

5×2=10

- (a) (i) Give one example each of electrode concentration cell and electrolyte concentration cell. 2
- (ii) Describe how the pH of a solution can be measured with the help of a hydrogen electrode. 3
- (b) Derive an expression for the e.m.f. of a concentration cell with transference. 5
- (c) (i) Derive an equation showing the effect of electrolyte concentration on electrode potential. 3
- (ii) Write Nernst equation and calculate e.m.f. of the following cell at 298 K : 2



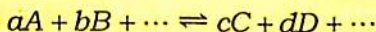
$$\text{Given, } E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$$

UNIT—III

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

3×3=9

- (a) Derive an expression for the change of Gibbs' potential for the following gaseous reaction : 3



(b) State and explain Le Chatelier's principle. 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

