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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

1×5=5

1. Select the correct answer :

   (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*

(Turn Over)

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

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

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

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

(iv) 908 mho cm^2 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

$$Fe + Zn^{2+} \rightarrow Zn + Fe^{2+}$$

is −0·35 V. The given cell reaction is

(i) feasible

(ii) not feasible

(iii) in equilibrium

(iv) not predictable

(Continued)

(e) The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75 J mol^{-1} 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 $-2{\cdot}5\times10^3$ cal and 7·4 cal deg^{-1} respectively. Determine whether the reaction is spontaneous or not at 298 K.

(Turn Over)

UNIT—I

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

(Continued)

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. 1½+1½=3

(Turn Over)

UNIT—III

5. Answer any *two* of the following questions : $5 \times 2 = 10$

(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* ? $2+3=5$

(Continued)