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4 SEM TDC CHM M 1

2014

(May)

CHEMISTRY

(Major)

Course : 401

(Physical Chemistry—I)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Select the correct answer : 1×5=5

(a) The correct order of the mobility of the alkali metal ions in aqueous solution is

(i) $K^+ > Rb^+ > Na^+ > Li^+$

(ii) $Rb^+ > K^+ > Na^+ > Li^+$

(iii) $Li^+ > Na^+ > K^+ > Rb^+$

(iv) $Na^+ > K^+ > Rb^+ > Li^+$

(b) The conductivity of a saturated solution of $BaSO_4$ is $3{\cdot}06 \times 10^{-6}$ ohm^{-1} cm^{-1} and its equivalent conductance is $1{\cdot}53$ ohm^{-1} cm^2 eq^{-1}. The solubility product of $BaSO_4$ will be

(i) 4×10^{-12}

(ii) $2{\cdot}5 \times 10^{-9}$

(iii) $2{\cdot}5 \times 10^{-13}$

(iv) 4×10^{-6}

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

(i) $6{\cdot}02 \times 10^{23}$

(ii) $3{\cdot}01 \times 10^{23}$

(iii) 2

(iv) $6{\cdot}02 \times 10^{-23}$

(d) For a spontaneous reaction, ΔG, equilibrium constant K and E°_{cell} will be respectively

(i) –ve, >1, +ve

(ii) +ve, >1, –ve

(iii) –ve, <1, –ve

(iv) –ve, >1, –ve

(Continued)

(e) The equilibrium constant K for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ at room temperature is 2·85 and at 698 K, it is $1{\cdot}4 \times 10^{-2}$. This implies that the forward reaction is

(i) exothermic

(ii) endothermic

(iii) neither exothermic nor endothermic

(iv) unpredictable

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

(a) The resistance of $N/10$ solution is found to be $2{\cdot}5 \times 10^3$ ohms. Calculate the equivalent conductance of the solution if the cell constant is $1{\cdot}15\ cm^{-1}$.

(b) Why does the variation of equivalent conductivity on dilution of a strong electrolyte differ from that of a weak electrolyte?

(c) In conductometric titration, the titre should be always very much concentrated than the solution to be titrated. Explain.

(d) Describe standard hydrogen electrode.

(e) Give one example each of electrode concentration cell and electrolyte concentration cell.

(f) Use of NH_4NO_3 in agar bridge minimizes the liquid junction potential. Explain.

(g) Show that

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_1, n_2, \ldots} = \overline{V}_i$$

(h) Calculate the e.m.f. of the cell

$$Ag\,(s)\,|Ag^+\,(a = 0{\cdot}1)\,||Zn^{2+}\,(a = 0{\cdot}1)\,|Zn\,(s)$$

given that the reduction potentials of Ag and Zn electrodes are 0·799 V and –0·763 V respectively. Is the reaction spontaneous?

UNIT—I

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

(a) (i) Represent the variation of equivalent conductance of KCl and CH_3COOH with dilution graphically and give explanation for such variation. 4

(ii) 0·1 (*N*) solution of sodium acetate was placed between two electrodes which were 0·72 cm apart and each has a cross-section 2·25 cm^2. The resistance of solution was 52·40 ohms. Find the specific and equivalent conductance. 1½+1½=3

(b) (i) What are Wien effect and Debye-Falkenhagen effect? 1½+1½=3

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

(c) (i) Explain how the transference number of an ion can be determined by moving boundary method. 4

(ii) The speed ratio of silver and nitrate ions in a solution of silver nitrate electrolysed between silver electrodes is 0·916. Find the transference number of the silver and nitrate ions. 1½+1½=3

UNIT—II

4. Answer any *two* 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 one difference between galvanic cell and electrolytic cell. 1

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

(ii) The e.m.f. of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298 K is 0·4188 V. If the pressure of the hydrogen gas was maintained at 1 atm, calculate the pH and hydrogen ion activity in the solution. (E_{ref} = 0·2415 V) 2

(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

UNIT—III

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

(a) State Le Chatelier's principle and establish its applicability with the help of two reactions as example.

(b) Deduce the relationship between ΔG° and K_c of a reversible reaction.

(c) Discuss the effect of temperature and pressure on chemical potential.

(d) Derive Duhem-Margules equation.

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