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4 SEM TDC CHM M 1

2015

(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) In a salt bridge, KCl is used because

(i) K^+ and Cl^- are isoelectronic

(ii) K^+ and Cl^- have same transport number

(iii) KCl is a strong electrolyte

(iv) KCl forms a good jelly with agar-agar

(b) The specific conductance of a solution is $0{\cdot}03568\ ohm^{-1}\ cm^{-1}$ and when placed in a cell, the conductance is $0{\cdot}0268\ ohm^{-1}$. The cell constant is

(i) $0{\cdot}0751\ cm^{-1}$

(ii) $0{\cdot}330\ cm^{-1}$

(iii) $0{\cdot}3836\ cm^{-1}$

(iv) $1{\cdot}331\ cm^{-1}$

(c) Which of the following solutions can be safely stored in a copper vessel?

(i) $ZnSO_4$

(ii) $AgNO_3$

(iii) $AuCl_3$

(iv) All of the above

(d) If three Faradays of electricity is passed through the solution of $AgNO_3$, $CuSO_4$ and $AuCl_3$, the molar ratio of the cations deposited at the cathodes will be

(i) 1:1:1

(ii) 1:2:3

(iii) 3:2:1

(iv) 6:3:2

(e) If K_p for a reaction

$$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$$

is 0·05 atm at 1000 K, then in terms of R its K_c will be

(i) $20000\ R$

(ii) $0{\cdot}02\ R$

(iii) $5 \times 10^{-5}\ R$

(iv) $\frac{5 \times 10^{-5}}{R}$

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

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

(b) State and explain Walden's rule.

(c) How will you determine the hydrolysis constant of aniline hydrochloride by conductance measurement?

(d) The standard reduction potential of Cu^{2+}/Cu electrode is 0·34 V. At what concentration of Cu^{2+} ions will the electrode potential be zero at 298 K?

(e) A nickel spatula cannot be used to stir a solution of copper sulphate. Explain the reason.

(f) Write the effect of temperature and pressure on chemical potential.

(g) Explain why the density of H_2SO_4 in a lead storage battery changes as it is charged.

UNIT—I

3. Answer any *two* from the following : $7 \times 2 = 14$

(a) (i) State Kohlrausch law of independent migration of ions. Explain how this law is helpful in determining the equivalent conductance of weak electrolyte at infinite dilution. 2+2=4

(ii) The molar conductances at infinite dilution of HCl, NaCl and NaZ (sodium crotonate) are 425×10^{-4}, 125×10^{-4} and 80×10^{-4} S m^2 mol^{-1} respectively. The specific conductance of 0·001 *M* aqueous solution of crotonic acid (HZ) is $3{\cdot}8 \times 10^{-3}$ S m^{-1}. Calculate the degree of dissociation of the acid. 3

(Continued)

(b) (i) What are the experimental evidences offered in support of the existence of ionic atmosphere surrounding an ion in an electrolytic solution? Discuss in detail. 4

(ii) What is meant by 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

(c) (i) Discuss the principle underlying the conductometric titrations. Sketch schematically the titration curves for the titration of a strong acid by a strong base and a weak acid by a strong base. 2+1+1=4

(ii) The specific conductance of a saturated solution of silver chloride at 25 °C after subtracting the specific conductance of water is $2{\cdot}28 \times 10^{-4}$ S m^{-1}. Calculate the solubility of silver chloride in grams per dm^3 at this temperature. Given, $\Lambda^{\circ}_{m\,(AgCl)} = 138{\cdot}3 \times 10^{-4}$ S m^2 mol^{-1} and $M_{(AgCl)} = 143{\cdot}5$ g mol^{-1}. 3

(Turn Over)

UNIT—II

4. Answer any *two* from the following : $5\times2=10$

(a) What is liquid junction potential? Derive an expression for liquid junction potential. How can it be minimized? $1+3+1=5$

(b) (i) What is a glass electrode? Describe how it can be used to measure the pH of a solution. 3

(ii) The e.m.f. of the following cell

$$Hg|Hg_2Cl_2, KCl(sat) \,||\, H^+(a_1)$$
quinhydrone/Pt

was found to be 0·228 V at 25 °C. Calculate the pH of the solution. (E_{cal} = 0·2415 V) 2

(c) (i) Derive an equation showing the effect of electrolyte concentration on electrode potential. 3

(ii) The standard e.m.f. of the Daniell cell involving the cell reaction

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

is 1·1 V. Calculate the equilibrium constant of the cell reaction at 25 °C. 2

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UNIT—III

5. Answer any *three* from the following : $3\times3=9$

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

$$aA + bB + \ldots \rightleftharpoons cC + dD + \ldots$$

(b) Derive Gibbs-Duhem equation for two-component system.

(c) For the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

K_p at 700 K was found to be $1{\cdot}6\times10^{-4}$, enthalpy change in this range of temperature is $-105{\cdot}3$ kJ mol^{-1}. Calculate K_p at 1000 K.

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

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