4 SEM TDC CHM M 1

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(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 : $1 \times 5 = 5$

    (a) Conductivity of $0 \cdot 01\,M$ NaCl solution is $0 \cdot 00147$ ohm^{-1} cm^{-1}. If extra 100 ml of water is added to the above solution, then this conductivity

    (i) increases

    (ii) decreases

    (iii) remains unchanged

    (iv) first increases and then decreases

(2)

(b) The precipitate of CaF_2 $(K_{sp}=1.7\times10^{-10})$ is obtained when equal volumes of the following are mixed

(i) 10^{-4} M Ca^{2+} and 10^{-4} M F^-

(ii) 10^{-2} M Ca^{2+} and 10^{-2} M F^-

(iii) 10^{-8} M Ca^{2+} and 10^{-3} M F^-

(iv) 10^{-10} M Ca^{2+} and 10^{-10} M F^-

(c) The amount of silver (atomic mass = 108) deposited from a solution of silver nitrate when a current of 965 coulombs was passed is
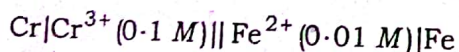
(i) 10·8 g

(ii) 0·108 g

(iii) 1·08 g

(iv) 1.08×10^3 g

(d) Given, $E^{\circ}_{(Cr^{3+}|Cr)}=-0.72$ V and $E^{\circ}_{(Fe^{2+}|Fe)}=-0.42$ V. The potential for the cell

$$Cr|Cr^{3+}(0.1\ M)|| Fe^{2+}(0.01\ M)|Fe$$

is

(i) −0·26 V

(ii) 0·26 V

(iii) 0·339 V

(iv) −0·339 V

(3)

(e) Which of the following equilibria is not affected by pressure changes?

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(iii) $2O_3(g) \rightleftharpoons 3O_2(g)$

(iv) $2NO_2(g) \rightleftharpoons N_2O_4(g)$

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

(a) Calculate the equivalent conductivity of 1 M H_2SO_4 solution whose conductivity is 26×10^{-2} ohm^{-1} cm^{-1}.

(b) Equivalent conductance of an electrolyte at finite concentration is less than that an infinite dilution. Explain.

(c) Explain why lithium ions move slower than potassium ions in water under an electric field.

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

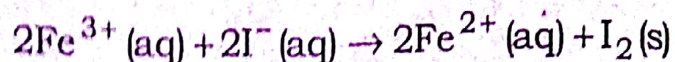(e) How will you prepare a normal calomel electrode?

(f) Write the chemistry of recharging of the lead storage battery, highlighting all the materials that are involved during discharging.

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(g) The cell in which the following reaction occurs

$$2Fe^{3+} (aq) + 2I^- (aq) \rightarrow 2Fe^{2+} (aq) + I_2 (s)$$

has $E^{\circ}_{cell} = 0\cdot236$ V at 298 K. Calculate the standard Gibbs' free energy of the cell reaction.

(h) What is fugacity? Write its physical significance.

UNIT—I

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

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

   (b) (i) Explain Kohlrausch law of independent migration of ions. The molar conductivities at infinite dilution of KCl, KNO_3 and $AgNO_3$ at 298 K are—

$$0\cdot01499 \ \Omega^{-1} \, m^2 \, mol^{-1};$$

                                 (Continued)