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3 (Sem–4/CBCS) CHE HC 3

2021

CHEMISTRY

(Honours)

Paper : CHE–HC–4036

(Physical Chemistry–III)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

GROUP–A

1. Answer the following questions : 1×5=5

   (a) Define molar conductivity of an electrolyte.

Contd.

(b) Equivalent conductance Λ_e and molar conductance Λ_m of $BaSO_4$ are related as — (*Choose the correct option*)

(i) $\Lambda_e = \frac{\Lambda_m}{2}$

(ii) $\Lambda_e = \Lambda_m$

(iii) $\frac{\Lambda_e}{2} = \Lambda_m$

(iv) $\Lambda_e = \frac{\Lambda_m}{4}$

(c) Write the Faraday's first law of electrolysis.

(d) Define Wien effect.

(e) Calculate dipole moment of *NaCl* is found to be 11.3 *D* and its experimental dipole moment is 8.5 *D*. Calculate the per cent ionic character of *NaCl*.

2. Answer the following questions : 2×5=10

(a) A current of 0.5 ampere is passed for 30 minutes through a voltameter containing copper sulphate solution. Calculate the weight of copper deposited at the cathode. (At. wt. of *Cu* = 63.6*u*).

(b) Explain how degree of dissociation of a weak electrolyte can be calculated from the measurement of conductance.

(c) For a salt of weak acid, show that the degree of dissociation is $\alpha = \sqrt{\left(\frac{K_w}{K_a.C}\right)}$.

The symbols signify the usual meanings.

(d) Write the electrode reactions and cell reaction for the following cell _____

$Pt, H_2(1atm) \mid HCl(c_1) \mid AgCl(s); Ag$

(e) For pH determination the quinhydrone electrode works satisfactorily only at _____ pH values.

3. Answer ***any three*** questions from the following : 5×3=15

(a) Define molar conductivity at infinite dilution. State and explain Kohlrausch law of independent migration of ions. 1+4=5

(b) Explain asymmetric effect and electrophoretic effect for strong electrolytes. Give Debye-Huckel-Onsagar equation for uni-uniequivalent electrolyte, explaining the terms involved in it. 3+2=5

(c) Give the conditions for a reversible cell. Give *one* example each of a reversible cell and irreversible cell. 3+2=5

(d) Name *two* metals that can be extracted by electrolysis method. With the help of a suitable example explain how electrolysis can be used in metallurgy. 1+4=5

(e) Define the terms dipole moment and molar polarisability. Explain why ethyl chloride has dipole moment of 2.05 *D* but chlorobenzene has the dipole moment of 1.70 *D*. 3+2=5

GROUP–B

4. Answer ***any three*** of the following : 10×3=30

(a) *(i)* Explain how equivalent conductivities of hydrochloric acid and acetic acid vary with concentration at constant temperature. The specific conductance of water at 298 K is $5.8\times10^{-8}\ S\,cm^{-1}$. Calculate the degree of dissociation of water. Given that Λ^0 for water at 298 K is 548.6 $S\ cm^2\ eq^{-1}$ and density of water is 0.997 $g\ cm^{-3}$. 3+2=5

(ii) What is drift velocity of ions in solution ? Explain why H^+ ion has the highest mobility in aqueous solution. 2+3=5

(b) *(i)* Explain the term transference number of ions. Explain the Hittorf's method of measurement of transference number of ions. Give the basis for calculation of transference number of ions in the Hittorf's method. 1+5=6

(ii) A solution of hydrochloric acid was electrolysed in a transport cell using platinum electrode. Analysis of cathode solution gave the following results :

Mass of Cl^- ions before electrolysis = 0.160 *g* per 20 *g* of water.

Mass of Cl^- ions after electrolysis = 0.146 g per 20 *g* of water.

A silver coulometer connected in series showed a deposit of 0.28 *g* of *Ag*.

Calculate the transport number of Cl^- ions.

(eq.wt. of *Cl* = 35.5 $g\ eq^{-1}$; *eq*. wt. of *Ag* =107.8 $g\ eq^{-1}$) 4

(c) (i) The equivalent conductivities of *HCl*, *NaCl* and CH_3COOH at infinite dilutions are 426.16, 126.45 and 91.0 $S\ cm^2\ eq^{-1}$ respectively. If the degree of dissociation of 0.1*N* acetic acid 0.001, calculate the equivalent conductance of acetic acid at this concentration. 4

(ii) Mention *two* advanatges of conductometric titration. Explain the variations of conductivity against volume of base added for the following conductometric titrations : HCl vs NH_4OH and acetic acid vs $NaOH$. 2+2+2=6

(d) (i) Define standard reduction potential. Represent the standard hydrogen electrode with its potential. With the help of a suitable example explain how standard reduction potential of any other electrode can be measured. 1+1+4=6

(ii) Explain how $\Delta G^o, \Delta H^o$ and ΔS^o of a cell reaction can be determined from the measurement of standard *emf* of a cell. 4

(e) (i) Explain the principle of acid-base titrations by potentiometric method. 6

(ii) Explain a method of measurement of magnetic susceptibility of a substance. 4