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4 SEM TDC CHM M 1 (N/O)

2019

(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. Choose the correct answer : 1×5=5

(a) The efficiency of a heat engine working between 273 K and 373 K is

(i) 26.8

(ii) 1.0

(iii) 0.366

(iv) 0.268

- (b) The amount of charge required for reduction of 1 mole of Cu^{2+} to Cu is
- (i) 96500 C
 - (ii) 48250 C
 - (iii) 193000 C
 - (iv) 24125 C
- (c) Which of the following statements is not true for conductometric titrations?
- (i) Coloured solutions can be titrated.
 - (ii) No indicator is required.
 - (iii) A strong acid can be titrated with a strong base.
 - (iv) A weak acid can be titrated with a weak base.
- (d) A cell reaction occurs spontaneously, if
- (i) ΔG is negative, E_{cell} is positive
 - (ii) ΔG is positive, E_{cell} is negative
 - (iii) both ΔG and E_{cell} are positive
 - (iv) both ΔG and E_{cell} are negative
- (e) The electrode that is not suitable for determining the pH of a strongly basic solution is
- (i) calomel electrode
 - (ii) glass electrode
 - (iii) quinhydrone electrode
 - (iv) hydrogen electrode

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

- (a) Show that entropy is produced in the irreversible process.
- (b) Explain the variation of specific and molar conductance with dilution.
- (c) Explain why Cd^{2+} ion in aqueous CdI_2 solution shows abnormal transference number.
- (d) Explain how the use of NH_4NO_3 in agar bridge minimizes the liquid-junction potential.
- (e) How do you prepare a normal calomel electrode?

3. Answer any two questions from the following : 4½×2=9

- (a) Deduce an expression for efficiency of a Carnot engine working between two temperatures T_1 and T_2 .
- (b) For one mole of an ideal gas, derive the expression for entropy change due to simultaneous changes in temperature and volume.
- (c) Prove that entropy of mixing of two or more ideal gases is always positive.

4. Answer any two questions from the following : 7×2=14

(a) (i) What do you mean by transference number of ions? Discuss the moving boundary method for determination of transference number of ions. 1+4=5

(ii) A saturated solution of AgCl at 20 °C has a conductivity of $3.41 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. The conductivity of water used was $1.60 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$. Determine the solubility of AgCl.

(Given, $\lambda_{\text{Ag}^+}^\circ = 61.92 \text{ ohm}^{-1} \text{ cm}^2$,
 $\lambda_{\text{Cl}^-}^\circ = 76.34 \text{ ohm}^{-1} \text{ cm}^2$) 2

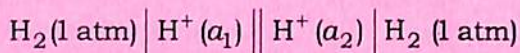
(b) (i) Explain with a suitable example how a precipitation reaction can be studied by conductometric titration. 2

(ii) Define cell constant. What is its unit? Explain how cell constant of a particular conductivity cell can be measured. The specific conductivity of an N/10 solution of KCl at 25 °C is $0.002765 \text{ mho cm}^{-1}$. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant? 1+½+2+1½=5

- (c) (i) Explain the variation of strong electrolyte with concentration in the light of asymmetry effect and electrophoretic effect. 4
- (ii) Explain why graphical method fails to determine molar conductance at infinite dilution for weak electrolytes. How can molar conductance at infinite dilution for weak electrolyte be measured? 1+2=3

5. Answer any two questions from the following : 5×2=10

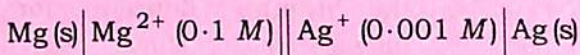
- (a) (i) What are concentration cells? Derive an expression for EMF of the following electrolyte concentration cell : 1+3=4



- (ii) Draw the potentiometric titration curve involving strong acid and strong base. 1
- (b) (i) What is hydrogen electrode? How can pH of a solution be measured with the help of hydrogen electrode? 1+3=4
- (ii) Define liquid-junction potential. 1

- (c) (i) What are storage cells? Discuss the charging-discharging processes in a lead storage cell. 1+2=3

- (ii) Calculate the EMF of the following cell : 2



Given,

$$E_{\text{Mg}^{2+} \mid \text{Mg}}^{\circ} = -2.37 \text{ V}$$

$$E_{\text{Ag}^+ \mid \text{Ag}}^{\circ} = 0.80 \text{ V}$$

(7)

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Choose the correct answer : 1×5=5

(a) The relation between equivalent conductance (Λ_e) and molar conductance (Λ_m) for $\text{Al}_2(\text{SO}_4)_3$ is

(i) $\Lambda_e = \Lambda_m$

(ii) $\Lambda_e = \frac{1}{2} \Lambda_m$

(iii) $\Lambda_e = \frac{1}{3} \Lambda_m$

(iv) $\Lambda_e = \frac{1}{6} \Lambda_m$

(b) The effect of high potential gradient on conductivity is known as

(i) asymmetry effect

(ii) electrophoretic effect

(iii) Wien effect

(iv) Debye-Falkenhagen effect

(c) A cell reaction occurs spontaneously, if

(i) ΔG is negative, E_{cell} is positive

(ii) ΔG is positive, E_{cell} is negative

(iii) both ΔG and E_{cell} are negative

(iv) both ΔG and E_{cell} are positive

- (d) The amount of charge required for reduction of 1 mole of Cu^{2+} to Cu is
- (i) 96500 C
 - (ii) 48250 C
 - (iii) 193000 C
 - (iv) 24125 C
- (e) For an ideal solution, the value of activity coefficient is
- (i) 0
 - (ii) 1
 - (iii) >1
 - (iv) <1

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

- (a) Explain the variation of specific and molar conductance with dilution.
- (b) Explain why transference number of Cd^{2+} shows abnormal behaviour in aqueous CdI_2 solution.
- (c) Write the differences between electrolytic and galvanic cells.
- (d) Explain how a standard hydrogen electrode is prepared.
- (e) What is fugacity? Write its physical significance.

1+1=2

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

(a) (i) Explain why graphical method fails to determine molar conductance at infinite dilution for weak electrolytes. How Kohlrausch's law is applicable for determination of such value? Explain with a suitable example. 2+2=4

(ii) What is cell constant? The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 ohm. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$? What is its molar conductance? 1+1+1=3

(b) (i) Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant? 3

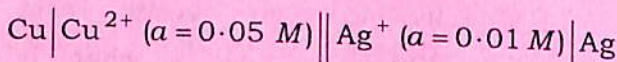
(ii) Write short notes on Wien effect and Debye-Falkenhagen effect. 2+2=4

- (c) (i) Define transference number of ions of an electrolyte. Calculate the transference number of H^+ and Cl^- from the following data obtained by moving boundary method, using $CdCl_2$ as the indicator electrolyte; concentration of HCl solution is $0.1 M$, mass of Ag deposited in the coulometer is $0.1209 g$, movement of boundary is $7.50 cm$ and cross-section of the tube is $1.24 cm^2$. $1+2=3$
- (ii) Define ionic mobility. Derive a relationship between ionic mobility and ionic conductance. $1+3=4$

4. Answer any two questions from the following : $5 \times 2 = 10$

(a) (i) What is meant by the term reference electrode? Explain with suitable example one oxidation-reduction electrode. $1+2=3$

(ii) Write electrode reaction and calculate the e.m.f. of the cell : 2



Given,

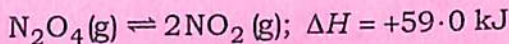
$$E_{Cu^{2+} | Cu}^{\circ} = -0.337 V$$

$$E_{Ag^+ | Ag}^{\circ} = 0.799 V$$

- (b) (i) Discuss how pH of a solution can be determined by using quinhydrone electrode. 4
- (ii) Draw the potentiometric titration curve involving strong acid and strong base. 1
- (c) (i) What is liquid-junction potential? How can it be minimized? $1\frac{1}{2}+1\frac{1}{2}=3$
- (ii) Discuss the charging-discharging processes in a lead storage cell. 2

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

- (a) State Le Chatelier's principle. Discuss the effect of change of temperature and pressure on the following equilibrium : $1+2=3$



- (b) Derive van't Hoff equation in the form

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2} \quad 3$$

(12)

- (c) Define activity and activity coefficient.
How can the behaviour of ideal and
non-ideal solution be determined from
activity coefficient? 1+1+1=3
- (d) Derive Gibbs-Duhem equation. 3
