

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 : 1×5=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

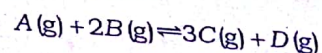
(iv) KCl forms a good jelly with agar-agar

(2)

- (b) The specific conductance of a solution is $0.03568 \text{ ohm}^{-1} \text{ cm}^{-1}$ and when placed in a cell, the conductance is 0.0268 ohm^{-1} . The cell constant is
- (i) 0.0751 cm^{-1}
 - (ii) 0.330 cm^{-1}
 - (iii) 0.3836 cm^{-1}
 - (iv) 1.331 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

(3)

- (e) If K_p for a reaction



is 0.05 atm at 1000 K, then in terms of R its K_c will be

- (i) $20000 R$
- (ii) $0.02 R$
- (iii) $5 \times 10^{-5} R$
- (iv) $\frac{5 \times 10^{-5}}{R}$

2. Answer any five of the following : $2 \times 5 = 10$

- (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 $\text{Cu}^{2+} / \text{Cu}$ electrode is 0.34 V. At what concentration of Cu^{2+} ions will the electrode potential be zero at 298 K?

(4)

- (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 $80 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ respectively. The specific conductance of 0.001 M aqueous solution of crotonic acid (HZ) is $3.8 \times 10^{-3} \text{ S m}^{-1}$. Calculate the degree of dissociation of the acid. 3

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(5)

- (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 $2.28 \times 10^{-4} \text{ S m}^{-1}$. Calculate the solubility of silver chloride in grams per dm^3 at this temperature. Given, $\Lambda_m^\circ(\text{AgCl}) = 138.3 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$ and $M_{(\text{AgCl})} = 143.5 \text{ g mol}^{-1}$. 3

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UNIT—II

4. Answer any two from the following :

5×2=10

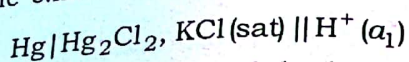
(a) What is liquid junction potential? Derive an expression for liquid junction potential. How can it be minimized?

1+3+1=5

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

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



quinhydrone/Pt

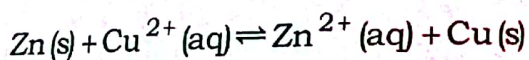
was found to be 0.228 V at 25 °C. Calculate the pH of the solution. ($E_{\text{cal}} = 0.2415 \text{ V}$)

2

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

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



is 1.1 V. Calculate the equilibrium constant of the cell reaction at 25 °C.

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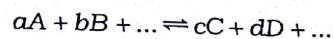
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UNIT—III

5. Answer any three from the following :

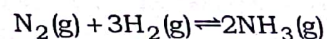
3×3=9

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



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

(c) For the reaction



K_p at 700 K was found to be 1.6×10^{-4} , enthalpy change in this range of temperature is $-105.3 \text{ kJ mol}^{-1}$. Calculate K_p at 1000 K.

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