2026

CHEMISTRY

(Major)

Paper : CHE0600304

(Equilibria and Electrochemistry)

Full Marks : 45

Time : 2 hours

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

1. Answer the following as directed : 1×5=5

(a) For a one-component system, the maximum number of phases that can exist in equilibrium is three.

(State True or False)

(b) An aqueous solution of Na_2CO_3 is basic. Explain.

(c) Under what conditions, pK_a is equal to the pH of solution?

(d) How does equivalent conductance vary with dilution?

(e) Nernst distribution law is used to

(i) determine the extent of dissociation or association in a solvent

(ii) determine the solubility of a solute in a solvent

(iii) study equilibrium of reactions involving complex ions

(iv) All of the above

(Choose the correct answer)

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

(a) State the law of mass action. Derive the expression of equilibrium constant for a general reaction $aA + bB \rightleftharpoons mM + nN$.

(b) State and explain the phase rule for a non-reactive system.

(c) What is meant by azeotropic mixture? Explain why azeotropes are not considered as definite compounds.

(d) The molar conductances at infinite dilution of NaOH, NaCl and $BaCl_2$ are $2 \cdot 48 \times 10^{-2}$ $Sm^2\ mol^{-1}$, $1 \cdot 27 \times 10^{-2}$ $Sm^2\ mol^{-1}$ and $2 \cdot 8 \times 10^{-2}$ $Sm^2\ mol^{-1}$ respectively. Calculate the molar conductance of $Ba(OH)_2$ at infinite dilution.

(e) Can there be a quadruple point on a phase diagram of a one-component system? Explain.

(f) Explain the following :

(i) Relaxation effect

(ii) Electrophoretic effect

(g) Which out of silver and aluminium metal is capable of displacing H_2 when dipped in HCl? Given that—

$$E^\circ_{Ag^+/Ag} = +0 \cdot 80\ V \text{ and } E^\circ_{Al^{3+}/Al} = -1 \cdot 66\ V$$

(h) With the help of Le Chatelier's principle, work out the condition which would favour the formation of ammonia in the following reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),\ \Delta H = -99 \cdot 38\ kJ$$

(i) In the precipitation of cations of group II of qualitative analysis, H_2S gas is passed through acidified solution of the salt by HCl. Explain using common-ion effect.

(j) State Nernst distribution law. Under what conditions is the law valid?

3. Answer any *four* of the following questions : 5×4=20

(a) Derive van't Hoff equation. Discuss the effect of temperature on K_P. 3+2=5

(b) Draw and interpret the phase diagram of water system.

(c) For a weak monobasic acid, show that the degree of ionization at a given temperature is inversely proportional to the square root of the initial concentration of the acid.

(d) What is buffer action? Derive the Henderson-Hasselbalch equation for a buffer mixture of weak acid and its salt. 1+4=5

(e) What is meant by electrochemical series? Can a solution of 1 *M* $CuSO_4$ solution be stored in a nickel metal vessel? Explain. Given that—

$E^\circ_{Ni/Ni^{2+}} = +0 \cdot 25$ V and $E^\circ_{Cu/Cu^{2+}} = -0 \cdot 34$ V

1+4=5

(f) Derive Gibbs - Duhem - Margules equation.

(g) What is ionic mobility? The H^+ ion, because of its heavy hydration and consequent large size should have low mobility, but the mobility of H^+ ion is very high. Explain. 1+4=5

(h) Explain how ionic product of water can be determined with the help of conductance measurement.

4. Answer any *one* of the following questions : 10

(a) (i) Define pH of a solution. Calculate the pH of a solution obtained by mixing 50 mL 0·2 mol dm^{-3} HCl solution with 50 mL 0·1 mol dm^{-3} NaOH solution at 298 K. Give the limitations of pH scale. 1+3+1=5

(ii) Calculate the solubility of $Mg(OH)_2$ in pure water at 298 K. Given, K_{sp} for $Mg(OH)_2$ at 298 K is $1{\cdot}20 \times 10^{-11}$. 3

(iii) Explain the application of buffer solutions in qualitative analysis of salt sample. 2

(b) (i) Derive Clausius-Claypeyron equation for liquid-vapour equilibria. 5

(ii) What is eutectic point? Draw and explain the phase diagram of lead-silver system with a eutectic mixture of composition 2·6% of Ag. The melting points of silver, lead and the eutectic mixture are 961 °C, 327 °C and 303 °C respectively. 1+4=5

(c) Derive the expressions for E_{cell} of an electrolyte concentration cell—

(i) with transference;

(ii) without transference.

What is the e.m.f. of a concentration cell consisting of two hydrogen electrodes represented as follows?

Pt, H_2(5 atm) | HCl (aq) | H_2(2·5 atm), Pt 8+2=10

(Continued)

(d) Discuss the principle of potentiometric titration for

(i) acid-base titration;

(ii) redox titration.

How would you titrate a solution of $AgNO_3$ against NaCl? 7+3=10

★ ★ ★