This question paper contains **8** printed pages]

Roll No.

(Write your Roll No. on the top immediately on receipt of this question paper.)

Attempt *six* questions in all, selecting at

least *two* questions from each Section.

Question No. **1** is compulsory.

Use of scientific calculator is allowed.

1.   Answer any *five* questions given below :   5×3=15

   (*a*)   How will you distinguish a compound and a eutectic mixture both of which have sharp

   melting points ?

   (*b*)   It is possible to cut through a slab of ice with a knife without separating the slab into

   two. Explain this observation using the phase diagram of water system.

(c) Explain whether the melting point of a solid substance be raised or lowered by applying pressure, if solid does not float on the liquid. Illustrate your explanation with the help of phase diagram.

(d) Tie lines connecting compositions of two phases in a three component system in which two components are partially miscible in each other and the third completely miscible are neither parallel to the side of the triangle or to each other. Why ?

(e) Explain the role of salt bridge in electrochemical cells.

(f) One way to prevent a buried iron pipe from rusting is to connect a piece of wire to a Mg or Zn rod. What is the electrochemical principle for this action ?

(g) Explain why we cannot use quinhydrone electrode to measure pH of a solution above 8.0.

Section A

2. (a) Derive Gibbs Phase Rule for a system in equilibrium in which one component is absent in a phase while other components are present in all phases.　　　　　　　　4

(b) A system of carbon tetrachloride (A) and dioxane (B) has two eutectic points—one at 247 K and 5 mol percent of B and the other at 253 K and 50 mol percent of B. A and B form a compound A_2B which melts congruently at 258. Pure A and B melt at 250 K and 285 K respectively. Construct the phase diagram of the system and label the lines and regions in the diagram. 5

(c) Descrbie the cooling curve of a two-component system in which the composition of the melt is equal to the eutectic composition. 3

3. (a) Derive Gibbs-Duhem-Margules equation. Show that in a binary solution if one component shows positive deviation then the other also does so. 4

(b) One mole of benzene is mixed with two moles of toluene at 60°C to form an ideal solution. The vapour pressure of benzene and toluene are 51.3 and 18.5 kPa respectively at this temperature. The pressure is gradually reduced. At what pressure will the vapour appear ? What will be the composition of the first bubble of the vapour ? 5

(c) Can phase rule be applied to a partially miscible two-component system ? How many degrees of freedom are required to describe such a system in which the system separates out into two distinct layers ? Is the system invariant above its CST ? Explain. 3

4. (*a*) State and explain Nernst Distribution Law and its limitations. 4

(*b*) A solute distributes itself between water and an organic solvent. It undergoes association in the organic solvent but remains unaffected in the aqueous phase. Comment on the degree of association of the solute in the organic phase from the following data : 4

Conc. in Aqueous Phase (g/L)	Conc. in Organic Phase (g/L)
0.6	1.98
0.9	9.76
1.3	18.57
1.7	31.47

(*c*) Establish that multistage extraction is more efficient than single stage process using the same amount of extracting solvent by taking the example of a system in which the distribution coefficient of the solute between an organic layer and aqueous layer is 2. 4

5. (*a*) Briefly explain the principle involved in fractional distillation of an ideal solution. 4

(*b*) Water and chloroform are partially miscible in each other while acetic acid is miscible in water and chloroform in all proportions. The solubility data curve of acetic acid water-chloroform at 298.15 K is given below. Plot the solubility curve of the system on a

triangular graph. If acetic acid is added to the system keeping the ratio of water to chloroform

constant at 1 : 2. What is the minimum percentage (wt/wt, %) of acetic acid that should

be present to obtain a single-phase system ?   5

Water (w/w, %)	Acetic acid (w/w, %)	Chloroform (w/w, %)
4.97	10.4	84.64
16.15	30.52	53.33
30.96	38.12	30.92
1.36	0.0	98.64
76.32	21.28	2.39
42.18	40.50	17.32
99.47	0.0	0.53

(c) Write a short note on steam distillation.   3
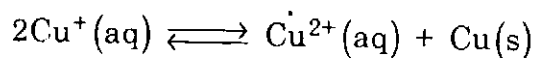
Section B

6. (a) What is emf ? Describe the method of measuring the emf of an electrochemical

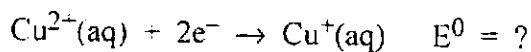cell.   3
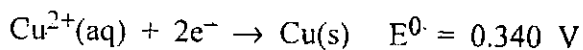
(b) The standard equilibrium constant for the reaction :

$$2Cu^+(aq) \rightleftharpoons Cu^{2+}(aq) + Cu(s)$$

at 298 K is 1.646×10^6. Construct the cell having the above cell reaction and calculate the standard potential of the cell.   4

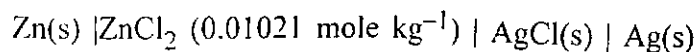(c) Compute E^0 for the reaction :   5

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu^+(aq) \quad E^0 = ?$$

Given :

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^0 = 0.340 \ V$$

$$Cu^+ + e^- \rightarrow Cu(s) \quad E^0 = 0.522 \ V.$$

7. (a) Write the electrode reactions, overall reaction and the Nernst equation of the cell used for the determination of pH formed by combining quinhydrone electrode with standard Calomel electrode.   3
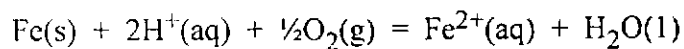
(b) The potential of the cell :

$$Zn(s) \ |ZnCl_2 \ (0.01021 \ mole \ kg^{-1}) \ | \ AgCl(s) \ | \ Ag(s)$$

is found to be 1.1566 V. Write down the cell reaction for the cell and what is the mean ionic activity coefficient of $ZnCl_2$.   5.

(c)   One of the reactions important in an acidic environment is :   4

$$Fe(s) + 2H^+(aq) + \tfrac{1}{2}O_2(g) = Fe^{2+}(aq) + H_2O(l)$$

Does the equilibrium constant favour the formation of Fe^{2+} (aq) ?

Given :

$$E^0_{Fe^{2+}/Fe} = -0.44 \text{ V}$$
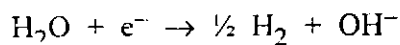
$$E^0_{H^+/O_2/Pt} = 1.23 \text{ V}$$

8.   (a)   Show that metal-metal ion electrode potential E_{Ag/Ag^+} is related to the corresponding

Metal-Insoluble salt-Anion electrode potential $E_{X^-/AgX/Ag}$ through the reaction :   4

$$E^0_{X^-/AgX/Ag} = E^0_{Ag^+/Ag} - \frac{2.303RT}{F} pK_{sp}(AgX)$$

where X^- are halide ions.

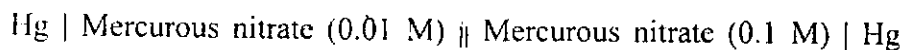(b)   Show that the standard potential of the reaction :

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^-$$

is given as

$$E^0 = \frac{RT}{F} \ln K_w$$

Determine its value at 298 K.   4

(*c*)   The emf of the cell :

Hg | Mercurous nitrate (0.01 M) ‖ Mercurous nitrate (0.1 M) | Hg
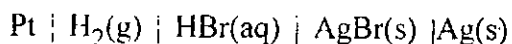
is found to be 0.0295 V at 25°C. Determine the molecular formula of mercurous

nitrate.   4

9.   (*a*)   What are concentration cell with and without transport. Give suitable examples. Derive

the potential for any one of them.   4

(*b*)   The standard cell potential of :

Pt ¦ H_2(g) ¦ HBr(aq) ¦ AgBr(s) ¦Ag(s)

was measured over a range of temperatures and the date were fitted to the following

relation.

$$E^0/V = 0.07131 - 4.99 \times 10^{-4}(T/K - 298) - 3.45 \times 10^{-6} (T/K - 298)^2$$

Evaluate the standard Gibbs energy, enthalpy and entropy change at 298 K.   4

(*c*)   Discuss the principle underlying potentionmetric titration. What are the advantages of

potentiometric titration ?   4