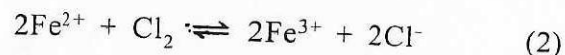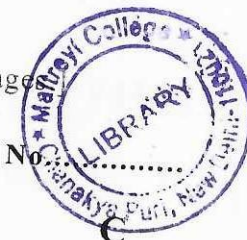(iii) Ascertain whether the following reaction will proceed in the (Vward or backward direction giving reasons.

$$2Fe^{2+} + Cl_2 \rightleftharpoons 2Fe^{3+} + 2Cl^-$$ (2)

(iv) Can a copper spoon be used to stir a solution of silver nitrate? Give reason.   (2)

This question paper contains 12 printed pages.

Your Roll No.

Sr. No. of Question Paper : 1419

Unique Paper Code : 32171303

Name of the Paper : Chemistry C-VII Physical Chemistry III: Phase Equilibria and Electrochemical Cells

Name of the Course : B.Sc. (H) Chemistry

Semester : III

Duration : 3 Hours

Maximum Marks : 75

Instructions for Candidates

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

2. Attempt **six** questions in all, selecting at least **two** questions from each section.

3. Question number **1** is compulsory.

4. Use of scientific calculator, log tables and graph paper is permitted.

$R = 8.314 \text{ J K}^{-1} \text{mol}^{-1}$ and $1 F = 96500 \text{ C mol}^{-1}$

$E^0_{Cd^{2+}|Cd} = -0.403\,V$; $E^0_{I^-|AgI|Ag} = -0.1522\,V$; $E^{\ominus}_{Fe^{2+}|Fe} = -0.44\,V$;

$E^{\ominus}_{Fe^{3+}|Fe} = -0.036\,V$; $E^{\ominus}_{Fe^{3+},Fe^{2+}|Pt} = 0.771\,V$; $E^{\ominus}_{Cr^{3+}|Cr} = -0.74\,V$

$E^{\ominus}_{Cd^{2+}|Cd} = -0.40\,V$; $E^{\ominus}_{Cl_2|Cl^-} = 1.3595\,V$; $E^{\ominus}_{Cu^{2+}|Cu} = 0.337\,V$; $E^{\ominus}_{Ag^+|Ag} = 0.799\,V$

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1. Answer any **five** questions given below :

    (i) How does the addition of naphthalene affect the CST of the phenol-water system at constant pressure. Explain giving reason. (3)

    (ii) Azeotropic mixtures have definite composition and definite boiling points yet they are not compounds. Explain. (3)

    (iii) Show that it is not possible to have more than three phases in equilibrium with each other in a one component system. What is the number of degrees of freedom when two phases are present? (3)

    (iv) Enthalpy of chemical adsorption of H_2 on the surface of Nickel is slightly positive yet the adsorption is spontaneous. Explain. (3)

    (v) Given the E° values for the electrodes $Fe^{2+}(aq)|Fe(s)$ and $Pt(s) |Fe^{3+}(aq), Fe^{2+}(aq)$ as -0.44 V and $+0.77$ V respectively, calculate the E° value for the electrode $Fe^{3+}(aq)|Fe(s)$. (3)

    (iii) Which of the following represents the variation of physical adsorption with 4 temperature? Explain your answer. (4)

9. (i) Given the cell,

    $Cd|Cd(OH)_2(s)|NaOH(0.01 \text{ mol kg}^{-1})\backslash H_2(1 \text{ bar})|Pt$
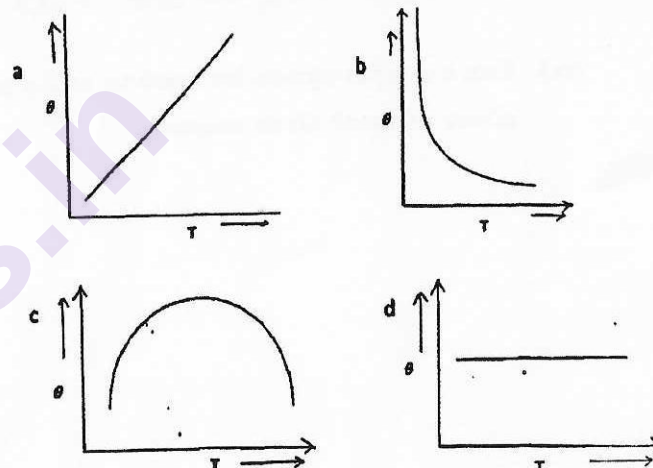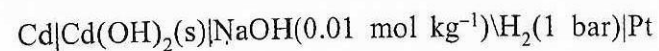
   With $E_{cell} = 0$ V at 298 K. Calculate the solubility product of $Cd(OH)_2$. (4)

    (ii) What are potentiometric titrations? Write the advantages of potentiometric titrations over conventional volumetric titrations. (4)

8.   (i)   For the cell $Pt|H_2(g, 1atm)|HBr(aq)|AgBr(s)|Ag(s)$

                                                                      (4)

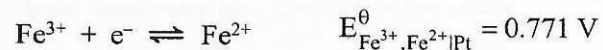E^0 cell$/V = 0.07131 - 4.99 \times 10^{-4}$ (T/K $- 298$) $- 3.45 \times 10^{-6}$ (T/K $- 298)^2$.

Evaluate change in standard reaction Gibbs energy, enthalpy and entropy at 298 K.

   (ii)   For the cell reaction,   (4)

$$2Fe^{3+}(aq) + Fe(s) \rightleftharpoons 3Fe^{2+}(aq)$$
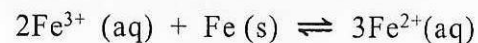
Construct two different galvanic cells using the following three half cells and calculate the standard cell potential for each of these cells. Compare the two cell potential values and comment on the result obtained.

Given :

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^{\theta}_{Fe^{2+}\backslash Fe} = -0.44$ V

$Fe^{3+} + 3e^- \rightleftharpoons Fe$ $E^{\theta}_{Fe^{3+}\backslash Fe} = -0.036$ V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^{\theta}_{Fe^{3+},Fe^{2+}|Pt} = 0.771$ V

  (vi)   How can liquid junction potential in a concentration cell be eliminated? Explain giving examples.   (3)

(vii)   Why can't we use a Voltmeter for determining the emf of a galvanic cell?   (3)

SECTION A

2.   (i)   Find the number of components in the following cases :

      (a) $HCl(g)$ and $NH_3(g)$ in equilibrium with $NH_4Cl(s)$ when the equilibrium is approached by starting with HCl and NH_3 only.

      (b) KCl-KBr-H_2O system.   (4)

  (ii)   Derive the Duhem-Margules equation from Gibbs-Duhem equation for a binary system.

                                              (4)

P.T.O.

(iii) On the basis of the critical temperatures, T_c of the gases given below, predict and explain which of the following gases will exhibit maximum adsorption on 1 g of charcoal at room temperature. (4)

Gas	CO_2	NH_3	H_2
T_c/ K	304	405	33

3. (i) Derive the relation between the number of phases (P), components(C) and degrees of freedom (F) for a non-reactive system in which one component is present in all but one phases, and another one is present in only two phases. Rest of the components are present in all the phases. (4)

(ii) Metals X and Y exhibit a simple eutectic diagram. Following table gives the break and halt points for various mixtures of X and Y.

$$\theta = \frac{(K.p)^{\frac{1}{2}}}{(1+K.p)^{\frac{1}{2}}}$$

where K is the equilibrium constant, p is the pressure and θ is the surface coverage. (4)

7. (i) Differentiate between Galvanic and electrolytic cells using appropriate diagrams. (4)

(ii) Calculate the liquid junction potential (E_{ljp}) associated with the following cell if the transference number of H^+ is 0.83.

Ag(s), AgCl(s), $HCl(m_1, \gamma_1)$: $HCl(m_2, \gamma_2)$, AgCl(s), Ag(s)

m_1=1.0 mol kg^{-1}; $\gamma_i = 0.809$; $m_2 = 0.05$ mol kg^{-1}; $\gamma_2 = 0.830$ (4)

(iii) How can the ionic product of water be determined using an electrochemical cell? Explain with the cell used, its reactions and the Nernst equation. (4)

SECTION B

6. (i) Construct a cell using the standard reduction potential values of the two half-cell reactions given.

$$Cr^{3+} + 3e^- \rightleftharpoons Cr$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$
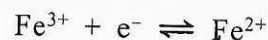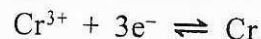
For the cell write (a) the cell reaction (b) Nernst equation.

Calculate the maximum work that can be obtained from the cell under the standard conditions.

(4)

(ii) The potential of the cell $Cd|CdI_2(a_2)|AgI(s)|Ag(s)$ is 0.286 V at 25°C. Calculate the mean ionic activity of the ions in solution and the activity of the electrolyte.

(4)

(iii) Derive Langmuir adsorption isotherm. Show that when a diatomic gas adsorbs as atom on the surface of a solid, the Langmuir adsorption isotherm becomes

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Mass % of Y	0	20	40	50	70	85	100
Break temp./°C	800	600	400	-	415	500	600
Halt temp. /°C	350	350	350	350	350	350	350

Draw the phase diagram and label all the regions.

What is the maximum percentage of Y that can be recovered by crystallization of a mixture containing 85% of Y?

(4)

(iii) What is the basic principle underlying steam distillation? A substance X, immiscible with water is distilled using this method. Derive an expression to calculate the relative mass of substances in the vapour phase in terms of their molar mass and vapour pressure.

(4)

4. (i) With a suitable derivation, show that a multistage solvent extraction is more efficient than a single stage extraction using the same amount of solvent.

(4)

(ii) To 100 mL of an aqueous solution of aspirin with concentration 3g / L, 50 mL of ether were added. The mixture was shaken and allowed to

P.T.O.

equilibrate at 293 K. The distribution coefficient of aspirin between ether and water is 5.9.

  (a) How much aspirin remains unextracted in the aqueous phase?

  (b) If instead of 50 mL ether, the extraction is carried out with two successive 25 mL portions of ether, how much aspirin remains unextracted?   (4)

(iii) Discuss how the extent of adsorption varies on (i) increasing the surface area per unit mass of adsorbent (ii) increasing the temperature of the system and (iii) increasing the pressure of the gas?   (4)

5. (i) Show that in a binary solution if one component behaves ideally then the other also does so.
                                                      (4)

  (ii) At 353 K, the vapour pressures of pure ethylene bromide and propylene bromide are 22.93 and

16.93 kPa, respectively, and these compounds form a nearly ideal solution. A mixture of 3 mol of ethylene bromide and 2 mol of propylene bromide is contained in a cylinder with a piston. Slowly the pressure is decreased.

  (a) Calculate the pressure at which the first bubble of vapour is formed.

  (b) How many moles of each compound is present in this bubble?

  (c) What is the composition of last droplet?
                                                      (4)

(iii) Define Critical solution temperature (CST). With the help of a suitable diagram, describe the sequence of steps that take place when the composition of a mixture of partially miscible liquids exhibiting lower C.S.T is varied at room temperature. Discuss with respect to the number of components, number of phases and degrees of freedom.   (4)