[This question paper contains 8 printed pages.]

Your Roll No. 2022

Sr. No. of Question Paper : 1373   C

Unique Paper Code   : 32171301

Name of the Paper   : Inorganic Chemistry II :
                        s- and p-Block Elements

Name of the Course   : **B.Sc. (H) Chemistry – CBCS (LOCF)**

Semester   : III

Duration : 3 Hours   Maximum Marks : 75

<u>**Instructions for Candidates**</u>

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

2.   Attempt **five** questions in all. Question number **1** is compulsory.

3.   **All** questions carry equal marks.

1.   Explain **any five** of the following, giving suitable reasons :

P.T.O.

(a) In spite of the ring strain in P_4 molecule, white phosphorus is stable relative to P_2.

(b) No reductant is required for the extraction of metals from HgO and Ag_2O.

(c) Helium and Neon do not form clathrate compounds.

(d) Carbon shows much greater tendency for catenation in comparison to silicon and nitrogen.

(e) The colour of halogens deepens down the group.

(f) Lithium forms predominantly the monoxide, sodium forms peroxide whereas potassium, rubidium and cesium form superoxides.

(g) Ionisation enthalpies of group 13 elements show irregular trends.

(3×5)

2. (a) Name the hydrides of group 15 elements and discuss the variation in their properties with reference to :

      (i) Basic character

      (ii) Thermal stability

      (iii) Reducing character

(b) Carbon is capable of reducing all metal oxides provided the temperature of reduction is sufficiently high, however the use of carbon as reducing agent becomes impractical for metal oxides towards the bottom of Ellingham diagram. Comment and also explain why most of the lines slope upwards in the Ellingham diagrams.

(c) Draw the structure of diborane and discuss the bonding involved using molecular orbital theory. Also, give experimental evidences in support of the structure.   (4,5,6)

3. (a) What is diagonal relationship? Giving at least three examples explain how boron resembles silicon.

    (b) Give the oxidation sates of sulphur in Caro's acid and Marshall's acid. Draw their structures and write one reaction by which both can be differentiated.

    (c) Arrange the following in the increasing order of their acidic strength and Justify your answer.

    (i) H_3PO_4, H_3PO_3, H_3PO_2

    (ii) HBr, HI. HCl, HF

    (iii) HClO, $HClO_3$, $HClO_2$, $HClO_4$ (4,5,6)
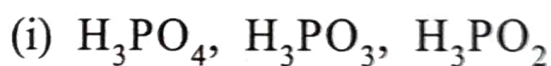
4. (a) Draw and discuss the structure of P_4O_{10} and write the mechanism for its hydrolysis.

(b) Discuss the structure of 3-dimensional silicates with reference to zeolites and their application as ion exchanger.
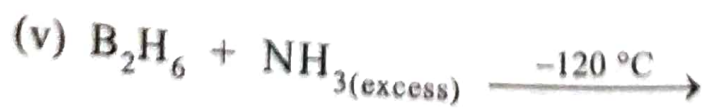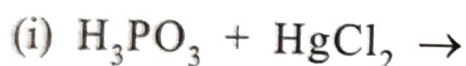
(c) Comment on any **three** :

    (i) XOX bond angle in Cl_2O is greater than that in F_2O.

    (ii) Cesium iodide is much less soluble in water than Cesium fluoride, but Lithium flouride is less soluble than Lithium iodide.

    (iii) Solubility of sulphates of alkaline earth metals decreases whereas it increases for their hydroxides on descending the group.

    (iv) Chlorine has greater electron gain enthalpy than fluorine, yet fluorine is a stronger oxidizing agent.

(v) Thallium doesn't exist in (III) oxidation state, yet TlI_3 exists. (4,5,6)

5. (a) Explain the dissimilarities between the two allotropic forms of carbon, namely graphite and diamond.

(b) Complete and balance the following equation : (any four)

(i) $H_3PO_3 + HgCl_2 \rightarrow$

(ii) $nPCl_5 + nNH_4Cl \xrightarrow{120-150\ °C}$

(iii) $B_3N_3H_6 + H_2O \xrightarrow{\Delta}$

(iv) $BCl_3 + LiAlH_4 \xrightarrow{ether}$

(v) $B_2H_6 + NH_{3(excess)} \xrightarrow{-120\ °C}$

(vi) $SiH_4 + AgNO_3 + H_2O \rightarrow$

(c) Draw the structure of **any three** :

    (i) Basic beryllium nitrate

    (ii) Mg-EDTA complex

    (iii) iodine heptafluoride

    (iv) 2,2,2-cryptand   (5,4,6)

6. (a) Discuss at least three points of similarities between halogens and pseudohalogens.

    (b) Alkaline earth metals are harder, denser and have high melting points as compared to alkali metals. Explain.

    (c) Write short notes on : **(any three)**

        (i) Cyanide Process

        (ii) Zone refining

        (iii) Interhalogen compounds

(iv) Solutions of alkali metal in liquid ammonia

(3,3,9)

[This question paper contains 8 printed pages.]

Your Roll No. 2022

Sr. No. of Question Paper : 1401   C

Unique Paper Code   : 32171302

Name of the Paper   : Organic Chemistry – II
(Oxygen Containing Functional Groups)

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 **five** questions in all.

1. (a) An organic compound A ($C_5H_{10}O_2$) on reduction with lithium aluminium hydride ($LiAlH_4$) forms organic compounds B (C_3H_8O) and C (C_2H_6O). B on oxidation followed by heating with calcium oxide gives D ($C_5H_{10}O$). C on reaction with NaOH/
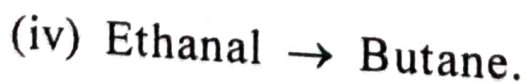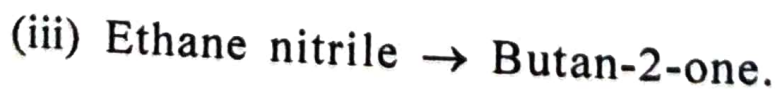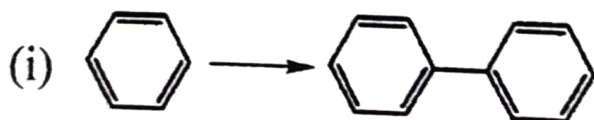
P.T.O.

b forms E and a yellow precipitate of CHI_3. Identify the organic compounds A, B, C, D and E. Give the name reaction involved during the conversion of C to E along with mechanism.
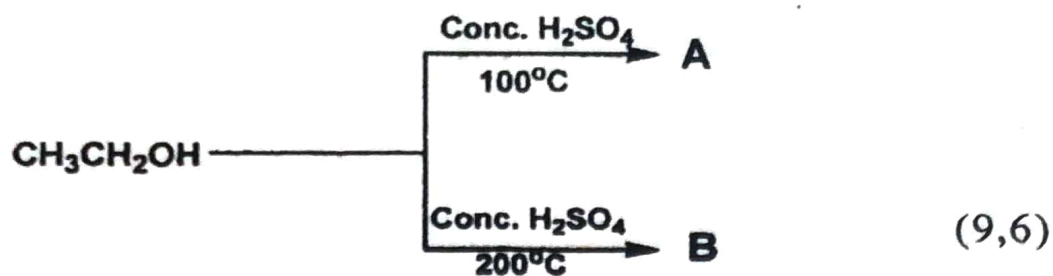
(b) Identify A having molecular formula $(C_{14}H_{12}O_2)$ in the following reaction. Give the name of the reaction and mechanism involved. Write down the role of cyanide ion in the following reaction :

(9,6)

2.   (a) Carry out the following conversions **(any three)** :

(i)

(ii) Propanal → Propan-2-ol.

(iii) Ethane nitrile → Butan-2-one.

(iv) Ethanal → Butane.

(b) Identify A and B in the following reaction and justify your answer :

$$CH_3CH_2OH \longrightarrow \begin{cases} \xrightarrow[100^\circ C]{\text{Conc. } H_2SO_4} A \\[2ex] \xrightarrow[200^\circ C]{\text{Conc. } H_2SO_4} B \end{cases}$$

(9,6)

3. (a) Carry out the synthesis of any three following compounds either from EAA (Ethyl acetoacetate) or DEM (Diethyl malonate) :

   (i) Methylsuccinic acid

   (ii) 4-Oxopentanoic acid

   (iii) Crotonic acid

   (iv) Antipyrine

   (b) Differentiate between the following (give visible test only) and write down the reaction involved **(any three)** :

   (i) Acetaldehyde and acetophenone

   (ii) Ethanol and propan-2-ol

   (iii) Benzoic acid and *p*-cresol

   (iv) Ethylchloride and chlorobenzene   (9,6)

4.   (a) Give reason for the following (any four) :

        (i) The rate of hydrolysis of the carboxylic acid derivatives is:

$$CH_3COCl > (CH_3CO)_2O > CH_3CONH_2$$

        (ii) S_N1 reactions are accompanied by racemization, while S_N2 reactions result in the inversion of the configuration.

        (iii) 2,2-Dimethylpropanal gives Cannizzzaro's reaction, while 2-methylpropanal does not.

        (iv) Carboxylic acid does not form oxime though they have carbonyl group ($>C=0$) in their structure.

   (v) Malonic acid and β-keto carboxylic acid decarboxlate readily on heating 200°C.

        (vi) Ketones cannot be prepared from acid chloride and RMgX although they can be prepared from acid chloride and R_2Cd/ R_2CuLi.

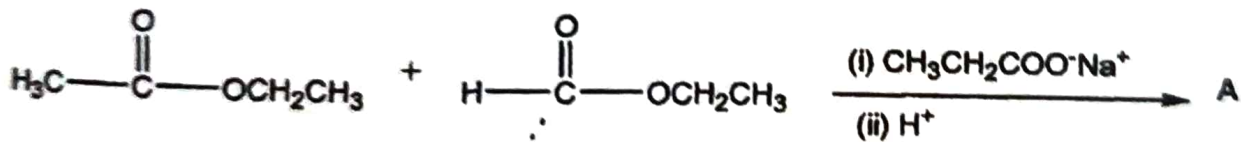   (b) Prepare the following organic compound using Wittig reaction :
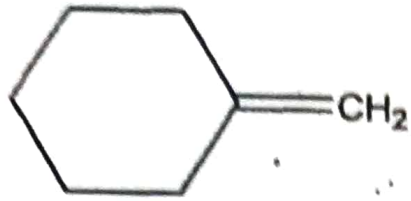
(12,3)

5. (a) Identify the organic compounds (A, B) and explain their formation with the help of mechanism.
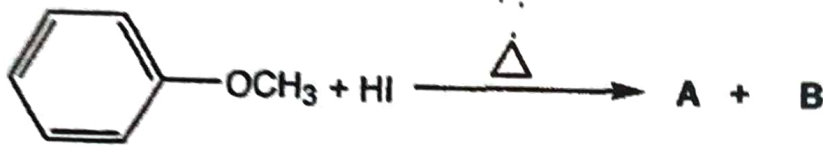
OR

Identify the organic compound (A) formed in the following reaction and explain its formation with the help of mechanism.
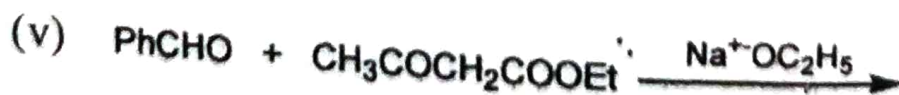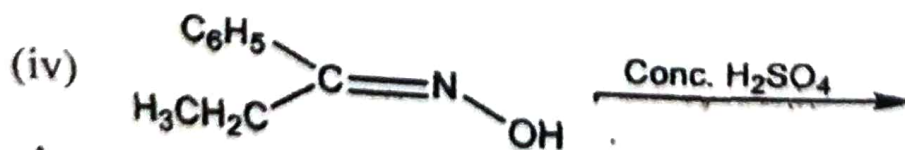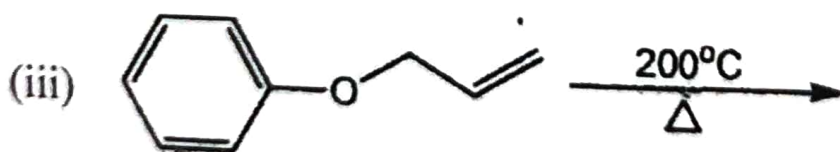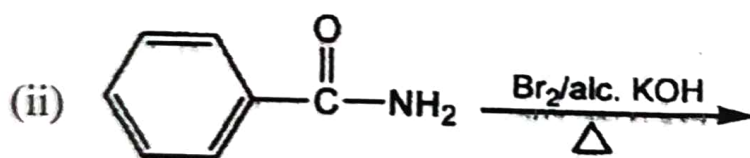

(b) Benzene on reaction with propene in the presence of a Lewis acid forms A (C_9H_{12}). A on aerial oxidation forms B ($C_9H_{12}O_2$). B on acidic hydrolysis gives C (C_6H_6O) and D (C_3H_6O). Identify the organic compounds A, B, C and D.

P.T.O.

(c) (i) Write down the products obtained on heating α, β and γ-hydroxycarboxylic acid separately.

(ii) Tertiary alkyl halides are not good substrates for nucleophilic substitution reactions. Explain.

(iii) p-Chlorotoluene on reaction with $NaNH_2$ in liq. NH_3 forms m-toluidine along with p-toluidine. Explain. (4,2,3,3,3)

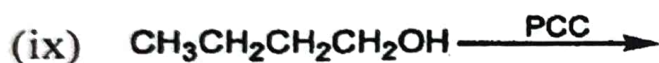6. Complete the following reactions :

(i) CH_3CH_2COOH $\xrightarrow{Cl_2/Red\ P}$

(ii)

(iii)

(iv)

(v) $PhCHO + CH_3COCH_2COOEt$ $\xrightarrow{Na^+OC_2H_5}$

(vi) $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_3 \xrightarrow{\text{Zn-Hg/HCl}}$

(vii)   [benzene ring with OH and COOH substituents] $\xrightarrow{\text{CH}_3\text{OH/H}^+}$

(viii) $CH_2\overset{\displaystyle COOC_2H_5}{\underset{\displaystyle COOC_2H_5}{}}$ + $\overset{\displaystyle H_2N}{\underset{\displaystyle H_2N}{}}C=O$ $\xrightarrow{\Delta}$

(ix) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{PCC}}$

(x) $CH_3CH_2CHO \xrightarrow[\text{(ii) } \Delta]{\text{(i) Dil. NaOH}}$

(xi) $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Br$ +   NaSH $\longrightarrow$

(xii)   [cyclopentanone ring with =O] $\xrightarrow{\text{CF}_3\text{COOOH}}$

(xiii) $H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-Br \ + \ CH_3O^-Na^+ \ \longrightarrow$

(xiv) $\underset{\underset{\displaystyle CH_2COOH}{|}}{CH_2COOH} \quad \overset{\Delta}{\longrightarrow}$

(xv) $\underset{\underset{\displaystyle CHO}{|}}{CHO} \quad \xrightarrow{\text{Conc. NaOH.}}$

(15)
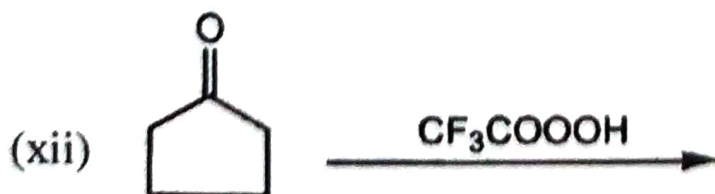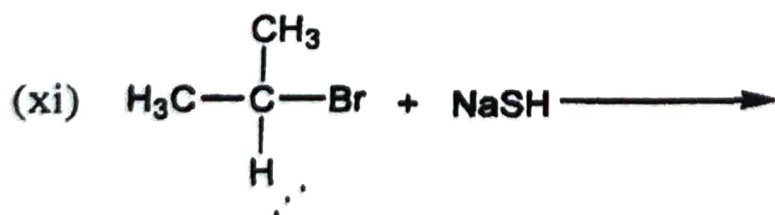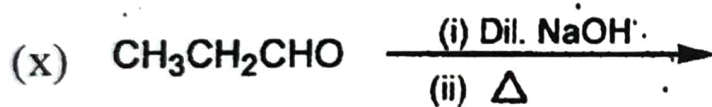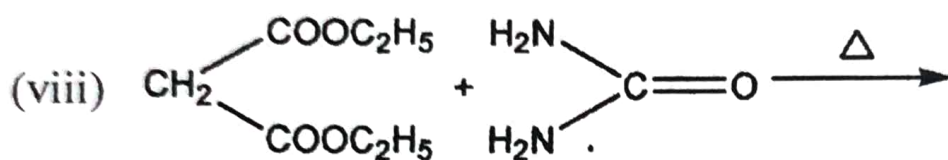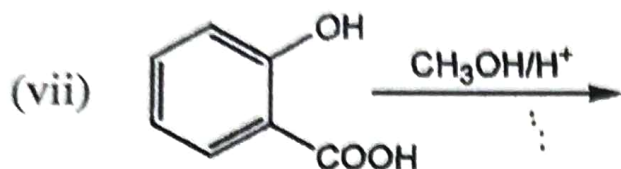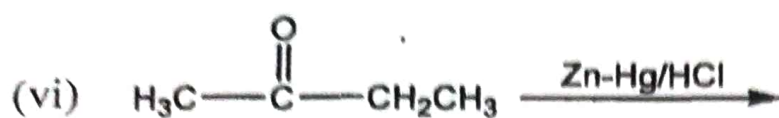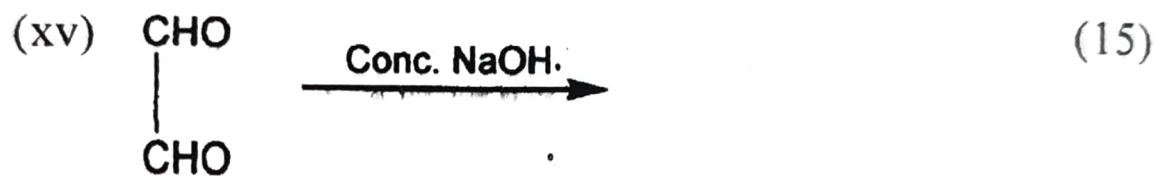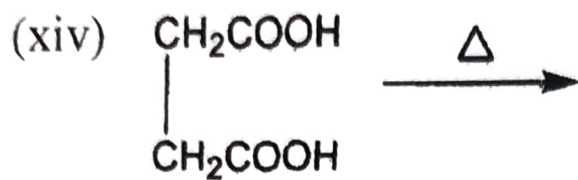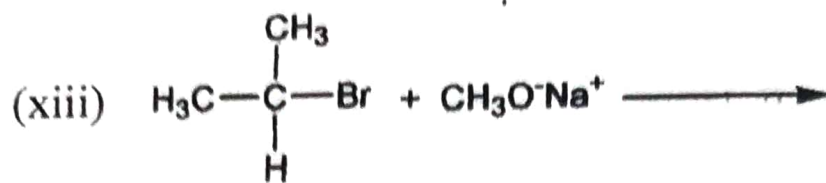
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Your Roll No. 2022

Sr. No. of Question Paper : 1419   C

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.

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

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

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

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

P.T.O.

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)

(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)

(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.

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

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)

SECTION B

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

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

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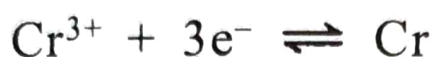
For the cell write (a) the cell reaction (b) Nernst equation.

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

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

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, γ_1): HCl(m_2, γ_2), AgCl(s), Ag(s)
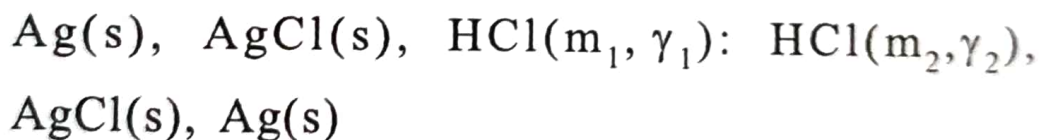
$m_1 = 1.0$ mol kg^{-1}; $\gamma_i = 0.809$; $m_2 = 0.05$ mol kg^{-1}; $\gamma_2 = 0.830$ (4)
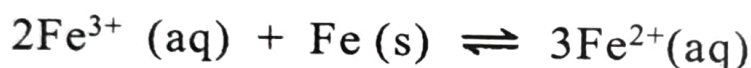
(iii) How can the ionic product of water be determined using an electrochemical cell? Explain with the cell used, its reactions and the Nernst equation. (4)

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

                                                           (4)

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

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.
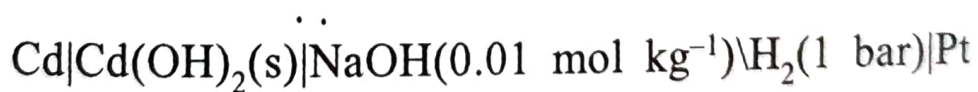
Given :

$$Fe^{2+} + 2e^- \rightleftharpoons Fe \qquad E^\theta_{Fe^{2+}\backslash Fe} = -0.44\text{ V}$$

$$Fe^{3+} + 3e^- \rightleftharpoons Fe \qquad E^\theta_{Fe^{3+}\backslash Fe} = -0.036\text{ V}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\theta_{Fe^{3+},Fe^{2+}|Pt} = 0.771\text{ V}$$

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

(4)

9.   (i) Given the cell,

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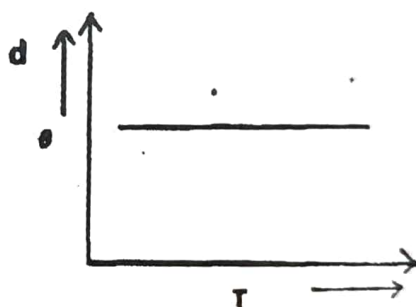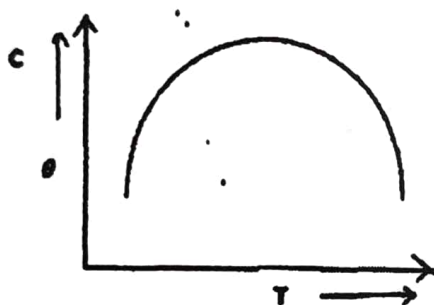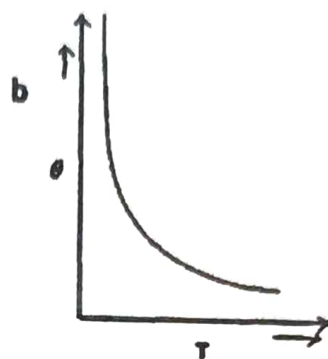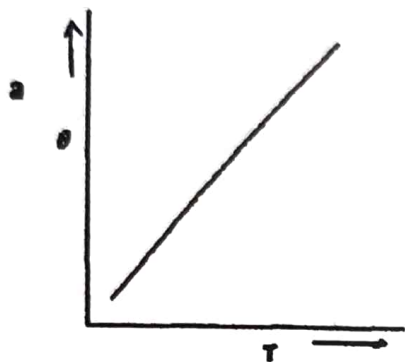
With $E_{cell} = 0$ V at 298 K. Calculate the solubility product of $.Cd(OH)_2$.

(4)

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

(4)

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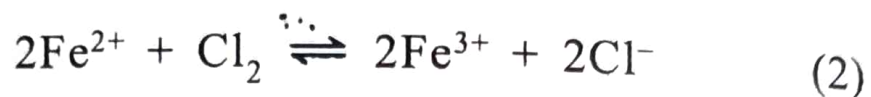
(iv) Can a copper spoon be used to stir a solution of silver nitrate? Give reason.   (2)