(13)

[This question paper contains 6 printed pages.]

Your Roll No...............

Sr. No. of Question Paper : 41   I

Unique Paper Code   : 32171301

Name of the Paper   : C-5; Inorganic Chemistry-II; s and p block elements

Name of the Course   : **B.Sc. (Hons) 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 any **five** questions.

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

1. Explain any **five** giving suitable reasons :

   (a) Phosphorus forms pentahalides whereas nitrogen and bismuth do not.

   (b) The boiling points of hydrides of group 16 follow the given trend :
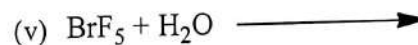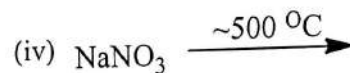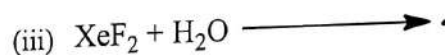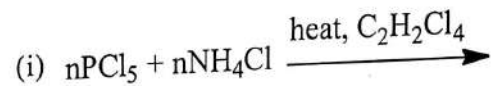
   $$H_2O > H_2S < H_2Se < H_2Te$$
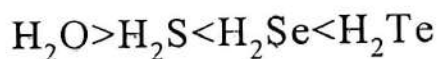
P.T.O.

(c) Ionization enthalpy of Li is very high and formation of N^{3-} requires ~2165 KJ/mole, still it forms Li_3N.

(d) Dilute solutions of alkali metals in liquid ammonia are paramagnetic and highly conducting.

(e) IF_7 is known while ICl_7 is not.

(f) $BeCO_3$ decomposes at about 100°C while the other group 2 carbonates require higher temperatures for decomposition.

(3×5)

2. (a) Draw and explain the structure of diborane with special reference to molecular orbital energy level diagram for the formation of B-H-B bonds.

(b) Magnesium metal burns in air to give an ash containing A and B. The ash on reaction with water gives an alkaline solution with smell of ammonia. Identify A and B with equations for the reactions.

(c) Explain the trend in solubility of hydroxides of alkali metals.

(d) The alkene and alkyne analogues of silicon are not known. Why?

(5,4,3,3)

3. (a) Complete and balance any **four** of the following reactions :

(i) $nPCl_5 + nNH_4Cl \xrightarrow{\text{heat, } C_2H_2Cl_4}$

(ii) $SiCl_4 + Li[AlH_4] \xrightarrow{\text{ether}}$

(iii) $XeF_2 + H_2O \longrightarrow$.

(iv) $NaNO_3 \xrightarrow{\text{~500 }^{O}C}$

(v) $BrF_5 + H_2O \longrightarrow$

(b) Which is stronger oxidizing agent in aqueous solution, fluorine or chlorine? Give suitable reasons.

(c) $SO_2(g)$ and $SO_3(g)$ have same hybridization but different structures. Explain.

(d) Mention the oxidation state of thallium in TlI_3 and name the compound. Justify the same. (6,3,3,3)

4. (a) Carbon monoxide is a better reducing agent for metal oxides than carbon below 983K but above this temperature, the reverse is true. Discuss with the help of Ellingham diagram and also mention the drawbacks of carbon as a reducing agent at high temperatures.

(b) Though ClO_2 is an odd electron molecule, it shows little tendency to dimerize. Why?

(c) Why do clay minerals cleave easily into thin sheets?

(d) HF is more ionic than HCl, but a weaker acid than HCl in aqueous solution. Why? (6,3,3,3)

5. (a) Write any one method of preparation of borazine. Though it is called inorganic benzene, it readily undergoes addition reactions unlike benzene. Explain with examples.

(b) $SnCl_2$ is a high melting solid whereas $SnCl_4$ is a liquid. Comment.

(c) Why does the first member of each group show anomalous behavior? Explain by taking Lithium as an example.

(d) Arrange the following oxoacids in the increasing order of their oxidizing power and justify the order :

$HClO$, $HClO_2$, $HClO_3$, $HClO_4$ (6,3,3,3)

6. (a) Draw and discuss structures of any **three** :

(i) Basic beryllium acteate.

(ii) Dibenzo-18-crown-6.

(iii) P_4O_{10}

(iv) $[Li (acac)_2]$

(b) Select the correct answer in each category with appropriate justification :

(i) Highest solubility in water: He, Ne, Xe

(ii) No flame coloration: Rb, Be, Cs

(iii) Paramagnetic species: O^{2-}, O_2^{2-}, O_2^-

(c) SiF_4 is readily hydrolyzed while CF_4 is not. Why? (6,6,3)

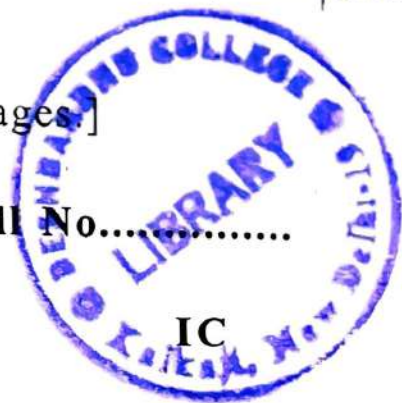7. Write short notes on any **three** : $5 \times 3 = 15$

(a) Peroxoacids of sulphur

P.T.O.

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(b) Vapour phase refining

(c) Clathrate compounds of noble gases

(d) Allotropes of phosporus

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[This question paper contains 4 printed pages]

Your Roll No.................

IC

Sr. No. of Question Paper : 42

Unique Paper Code : 32171302

Name of the Paper : C VI – Organic Chemistry – II

Name of the Course : **B.Sc. (Hons.) 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 any **five** questions.

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

1. (a) An organic compound **A** (C_4H_8O) reacts with hydroxylamine to give two isomeric compounds **B** and **C** (C_4H_9ON). Compound **B** and **C** when treated with sulphuric acid separately, give compounds **D** and E (C_4H_9ON) respectively. Identify **A, B, C, D** & E and write all the reactions involved. Name the reaction by which **B** is converted to **C** along with the mechanism.

(10)

P.T.O.

(b) Write one test with reaction involved for distinction between the following pairs of compounds.

   (i) Benzyl alcohol and phenol

   (ii) Acetaldehyde and acetone   (2×2.5)

2. How will you prepare the compounds **a, b, & c** from ethyl acetoacetate and **d & e** from diethyl malonate?   (5×3)

(a) 3-Methylpentan-2-one

(b) Pentane-1,5-dioic acid

(c) n-Butyric acid

(d) Adipic acid

(e) 5,5-Diethylbarbituric acid

3. Explain the following :   (5×3)

(a) Maleic acid is stronger than fumaric acid. However the second dissociation of fumaric acid occur more readily than maleic acid.

(b) S_N2 reactions involve complete inversion of configuration.

(c) Phenol is a weaker acid than p-nitrophenol.

(d) Vinyl chloride is less reactive than ethyl chloride towards nucleophilic substitution reactions.

(e) Methoxy benzene is prepared by reaction of methyl chloride and sodium phenoxide rather than from chlorobenzene and sodium methoxide.

4. Write the products for the following along with equations :   (5×3)

(a) When α-, β-, and γ- hydroxy acids are heated separately.

(b) Ethyl acetate is treated with sodium ethoxide followed by reaction with one mole of methyl iodide in the presence of sodium metal.

(c) Phenol is heated with chloroform in the presence of sodium hydroxide followed by reaction with alkaline $KMnO_4$.

(d) 2-Phenyl-1-ethanol is treated with dil. NaOH.

(e) Formic acid and malonic acid are hearted separately.

5. How will you carry out the following conversions?   (5×3)
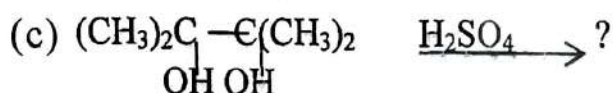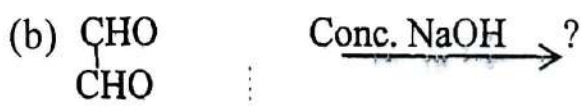
(a) Propanoic acid to lactic acid

(b) Phenol to aspirin

(c) Propanal to 2-butanol

(d) Phenylacetaldehyde to phenylacetamide

(e) Aniline to iodobenzene.

6. Complete the following reactions. Write the mechanism of the reaction involved. (3×5)

   (a) $C_6H_5CONH_2$ $\underrightarrow{Br_2/NaOH}$?

   (b) $\begin{array}{c} CHO \\ | \\ CHO \end{array}$ $\underrightarrow{Conc. NaOH}$?

   (c) $(CH_3)_2C\!\!-\!\!C(CH_3)_2$ $\underrightarrow{H_2SO_4}$?
   $\qquad\quad\ \ \overset{|}{O}H\ \overset{|}{O}H$

7. Write short notes on any **three** of the following with emphasis to (i) the functional group that undergoes these reactions, (ii) products formed, (iii) reaction conditions and (iv) mechanism. (3×5)

   (a) Benzoin condensation

   (b) Perkin reaction

   (c) Wittig reaction

   (d) Claisen rearrangement

   (e) Dieckmann reaction

(1800)

This question paper contains **7** printed pages]

Roll No.

S. No. of Question Paper : **43**

Unique Paper Code : **32171303**

Name of the Paper : **Physical Chemistry-III : Phase**

Equlibria, Electrochemical Cell

Name of the Course : **B.Sc. (Hons.) Chemistry**

Semester : **III**

Duration : **3 Hours** Maximum Marks : **75**

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

Question No. **1** is compulsory.

Attempt *six* questions in all,

selecting at least *two* questions from each Section.

Use of scientific calculator is permitted.

Graph paper may be provided.

Values of constant : $R = 8.314$ JK^{-1} Mol^{-1}; $F = 96500$ C Mol^{-1}.

P.T.O.

1. Attempt any *five* questions from the following :   5×3

(*a*) Why a saturated solution of KCl or NH_4NO_3 should be used in the salt bridge ?

(*b*) Polarities of cathode and anode in a galvanic cell are opposite to those in an electrolytic cell.

(*c*) Langmuir equation is more suitable for chemisorption than physisorption.

(*d*) Adsorption is an exothermic process.

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

(*f*) Find out the number of components present in the solution containing Na^+, Cl^-, Ag^+, NO_3^-, $AgCl(s)$ and H_2O.

Section-A

2. (*a*) The EMF of the following cell :

$$Cd/CdCl_2(satd.)//AgCl(s)/Ag$$

is 0.6753 V at 25°C and 0.6915 V at 0°C.
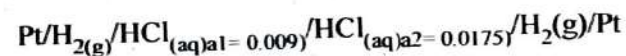
Calculate ΔG, ΔH and ΔS for the cell reaction at 25°C.

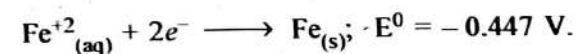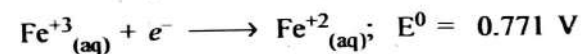(*b*) Derive an expression for the electrode potential for the following half cells :

(*i*) $Pt/H_2(g)/OH^{-1}_{(aq)}$

(*ii*) $CrO_4^-/Ag_2CrO_4/Ag$.
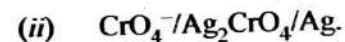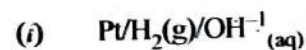
(*c*) Explain with examples, the difference between reversible cell and irreversible cells.   6,3,3

3. (*a*) Given the cell,

$$Pt/H_{2(g)}/HCl_{(aq)a1=0.009}/HCl_{(aq)a2=0.0175}/H_2(g)/Pt$$

$E_{cell} = 0.028$ V at 25°C

(*i*) Derive an expression for EMF of cell with transference.

(*ii*) Calculate the liquid junction potential associated with this cell. The transference no. of H^+ ions is 0.83.

(*b*) You are given the following reduction reactions and E^0 values :

$$Fe^{+3}_{(aq)} + e^- \longrightarrow Fe^{+2}_{(aq)}; \quad E^0 = 0.771 \text{ V}$$

$$Fe^{+2}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}; \quad E^0 = -0.447 \text{ V}.$$

Calculate E^0 for half cell reaction :

$$Fe^{+3}_{(aq)} + 3e^- \longrightarrow Fe_{(s)}.$$ 8,4
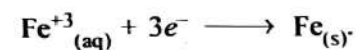
4. (a) Construct the appropriate cell and to determine the equilibrium constant for the reaction at 298 K :

$$Cd^{+2}_{(aq)} + 4NH_{3\ (aq)} \rightleftharpoons [Cd(NH_3)_4\ ]^{+2}$$
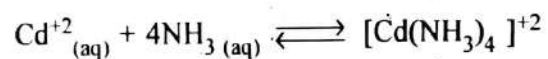
$E^0_{Cd^{+2}/Cd} = -0.40$ V and $E^0_{[Cd(NH_3)_4]^{+2}/Cd} = -0.61$ V.

(b) Explain, how the pH of a solution is determined by using the quinhydron electrode.

(c) What other electrodes can also be used to determine the pH of the solution ? 6,3,3

5. (a) Give the postulates on which Langmuir's adsorption isotherm is based and develop an expression for the same. What form does the equation take under conditions of low pressure and high pressure ?

(b) At 0°C and 1 atm pressure, volume of N_2 gas required to cover a sample of silica gel assuming Langmuir monolayer adsorption is found to be 130 cm^3 g^{-1} of the gel. Calculate the surface area per gram of silica gel. Given that the area occupied by a N_2 molecule is 0.162 nm^2. 6,6

Section-B

6. (a) Using Clausius-Clapeyron equation, draw the labelled phase diagram for water.

(b) A mixture of an organic liquid A and water is distilled under 1 atm pressure at 372.2 K. What mass of steam would be condensed to obtain 1 g of liquid A in the distillate ? The vapour pressure of H_2O at 372.2 K is 739 torr and molar mass of A = 123 g mol$^-$.

(c) What are the azeotrops ? Can they be purified by fractional distillation ? Justify your answer. 4,4,4

7. (a) Construct a well labelled phase diagram for zinc and magnesium system using the following data :

(i) Melting point of magnesium, 655°C

(ii) Melting point of zinc, 500°C

(iii) One eutectic point at 350°C with 20 mole per cent of zinc and another at 430°C with 92 mole per cent of zinc.

(*ii*) A solid compound of $MgZn_2$ is formed which melts congruently at 540°C.

Draw the cooling curves at 20% mole and 40% mole of Zinc.

(*b*) A solute distributes itself between two immiscible solvents α and β. If the solute was found to be associated in phase β while it remained unaffected in the other, find out the distribution coefficient of the solute between phase α and β.

(*c*) Starting from Duhem-Margules equation, show that if one component behaves ideally, the second component also behave in the ideal manner. 6,3,3

8. (*a*) Derive an expression of phase rule for the reactive and non-reactive system.

(*b*) When a liquid, which is immisible with water, was steam distilled at 95.2°C at a total pressure of 747.3 torr, the distillate contained 1.27 g of the liquid per gram of water. Calculate the molar mass of the liquid. The vapour pressure of water is 638.6 torr at 95.2°C.

(*c*) What is the effect of different types of impurities on CST ? Explain with examples. 4,4,4

9. Write short notes on any *three* :

(*a*) Calomel electrode

(*b*) Physical adsorption and Chemical adsorption

(*c*) BET equation

(*d*) Fractional distillation of ideal and non-ideal solutions. 4,4,4

[Type text]

SI-NO 07 G.P : 1590

Course: B.Sc. (H) Chemistry

Semester: III

Unique Paper Code: 217303

Name of paper: CHHT – 306: Organic Chemistry-II

M.Marks:75

Duration: 3 hours

Instructions for Candidates

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

2. Attempt any **six** questions.

3. All questions carry equal marks.

1. (a) An organic compound 'A'(C_4H_9Cl) on hydrolysis with aq. Alkali forms compound 'B' ($C_4H_{10}O$). 'B' on oxidation forms another compound 'C' which does not reduce Fehling's solution. On treatment with iodine and NaOH both 'B' and 'C' form iodoform. 'B' on dehydration with conc H_2SO_4 forms mainly compound 'D' which on ozonolysis forms two molecules of acetaldehyde. Identify A, B, C and D. Write the reactions involved. (8)

   (b) Write one test with reaction involved to distinguish the following pairs of compounds

   (i) Acetaldehyde and Acetone

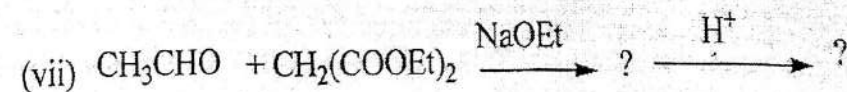   (ii) Acetone and Diethyl ketone   (4.5)

2. Explain why

   (i) Magnesium or Cadmium is not used in place of Zinc in Reformatsky reaction.

   (ii) Vinyl chloride is less reactive than ethyl chloride towards nucleophilic substitution reaction.

   (iii) The reactivity of aryl halide increases towards nucleophilic reaction with the substitution of -NO_2 group at *o*- and *p*-positions.

   (iv) Ketones can not be prepared from RCOCl and Grignard reagent (RMgX) although they can be prepared from RCOCl and R_2Cd.   (3,3,3,3.5)

3. Answer the following questions

(i) Give SN^2 reaction mechanism for nucleophilic substitution in alkyl halides.Also predict the stereochemistry of the product.

(ii) p-Chlorotoluene on reaction with NaNH$_2$ in liq.NH$_3$ gives formation of m-toluidine along with p-toluidine. Give reason with mechanism and also name of mechanism.

(iii) Write the product when benzaldehyde is treated with hydroxyl amine hydrochloride.Give the mechanism.

(iv) Which one out of primary, secondary and teritary halides is most reactive towards dehydrohalogenation reaction? Give reasons? (3,3,3,3.5)

(10)

4. (a) Complete the following reactions

(i) $C_6H_5CHO + HCHO \xrightarrow{\text{conc. KOH}} ? + ?$

(ii) $C_6H_5CHO + CH_3CHO \xrightarrow{\text{dil. NaOH}} ?$

(iii) $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Et \xrightarrow{\text{peracetic acid}} ?$

(iv) $CH_3COCH_3 + CH_3MgBr \longrightarrow ? \xrightarrow{H^+} ?$

(v) $C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow{\text{Eth. KOH}} ?$

(vi) $C_6H_5CHO \xrightarrow{\text{aq. eth. KCN}} ?$

(vii) $CH_3CHO + CH_2(COOEt)_2 \xrightarrow{\text{NaOEt}} ? \xrightarrow{H^+} ?$
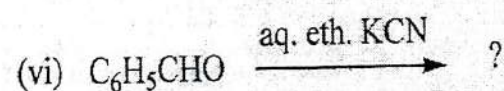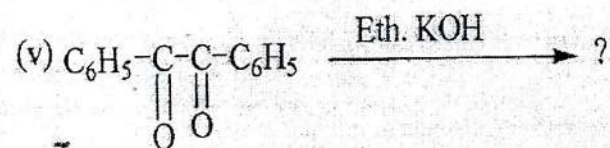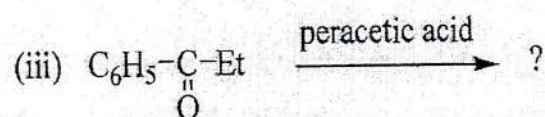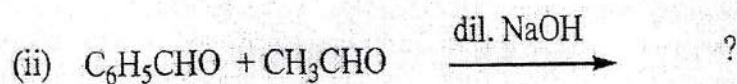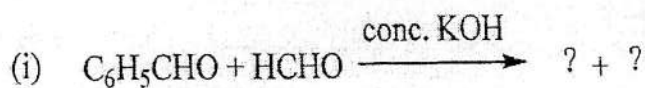
(b) The rate of addition of HCN to ketones to form cyanohydrins is increased by adding traces of NaCN.
Explain (2.5)

5 (a) Convert

(i) Acetone to 4-Methyl-3-penten-2-one

(ii) Acetaldehyde to 2-Hydroxypropanoic acid

(3,3)

(b) SN¹ reactions of alkyl halides proceed with partial racemization and inversion. Give reason.

(4)

(c) o-Hydroxybenzaldehyde has lower B.Pt as compared to its m- or p- isomers. Give reason

(2.5)

6. (a) Give the relative reactivity order of derivatives of carboxylic acids towards hydrolysis explain the order. (4)

(b) Maleic acid is stronger acid than fumaric acid. Explain. (2)

(c) How is tartaric acid synthesized from ethylene? (3)

(d) what is the effect of heat on α, β and y – hydroxyl acid ? Give the relevant reactions. (3.5)

7. (a) Write short note on any *three* of the following

   (i)   Perkin Reaction

   (ii)   Witting reaction

   (iii)   Michael Condensation

   (iv)   Haloform reaction   (3.5,3.5,3.5)

(b) Which characteristic reactions do aldehydes and ketones show?   (2)

Sl No. Q.P. 1591

| Unique Paper Code | : | 217305 |

| Name of the Paper | : | Physical Chemistry-II (CHHT- 307) |

| Name of the Course | : | B.Sc. (Hons.) 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.

3. Question No. 1 is compulsory.
   Gas constant, $R = 8.314 \, JK^{-1}mol^{-1} = 8.314 \, kPa \, dm^3 \, K^{-1}mol^{-1}$
   For monatomic ideal gas, $C_v = 3/2 \, R$, $C_p = 5/2 \, R$

Q1. Attempt any *five* of the following:
   (a) Osmotic pressure measurements are preferred to the other colligative properties to determine the molar mass of macromolecules. Give reason.
   (b) C_p is always greater than C_v.
   (c) Why ΔG is used more compared to ΔA to express the condition of spontaneity of the reaction?
   (d) What is enthalpy of neutralization? Why is its value same for all strong acids when they are neutralized with strong bases?
   (e) For mixing of two solvents to form an ideal solution, $\Delta V_{mix} = 0$.
   (f) The equilibrium constant K_p of a gaseous reaction is independent of pressure, K_x is not.
   (g) Why the synthesis of ammonia is preferably carried out at low temperature and high pressure? (Exothermic reaction)   (3 X 5)

Q2.
   (a) State the first law of thermodynamics. Show that change in internal energy, dU is an exact differential whereas dq and dw are not.
   (b) Prove that:
      (i) Joule –Thomson expansion is an isoenthalpic process.
      (ii) For an ideal gas, $\left(\frac{\partial H}{\partial V}\right)_T = 0$
   (c) One mole of an ideal monatomic gas at 298 K, occupying a volume of 3 dm^3 is expanded adiabatically and reversibly to a pressure of 101.325 kPa. Calculate q, w, ΔU, ΔH and ΔS.
                                                                                            (4,4,4)

Q3.
(a) Differentiate between:
   (i) Differential and Integral enthalpy of solution.
   (ii) Bond enthalpy and Bond dissociation enthalpy.

(b) State and explain Hess's law of constant heat summation. Hydrazine, N_2H_4 is a colourless liquid used as a rocket fuel. What is the enthalpy change for the process in which hydrazine is formed from its elements?

N_2 (g) + $2H_2$ (g) → N_2H_4 (l)

Use the following reactions and enthalpy changes:
   (i) N_2H_4 (l) + O_2 (g) → N_2 (g) + $2H_2O$ (l); $\Delta H = -622.2$kJ
   (ii) H_2(g) + ½ O_2 → H_2O (l); $\Delta H = -285.8$ kJ

(c) Derive Kirchhoff's relation to show the variation of heat of reaction with temperature at constant pressure.

(4, 4, 4)

Q4.
(a) State and explain third law of thermodynamics. How is it useful in calculating the absolute entropy of a substance?

(b) Deduce the entropy changes of an ideal gas in reversible adiabatic and irreversible isothermal processes. Also comment on the result.

(c) By using the third law of thermodynamics predict the absolute entropy of water at 0 K and use the same to compute the absolute entropy of water at 400 K and 1 bar pressure from the following data:

C_p (H_2O (s) ,0-273K) = 30 J K^{-1} mol^{-1}
C_p (H_2O (l), 273-373K) = 75 J K^{-1} mol^{-1}
C_p (H_2O (v) , 373- 400 K) = 36 J K^{-1} mol^{-1}
ΔH_{fusion} = 65 kJ mol^{-1}
ΔH_{vap} = 40 kJ mol^{-1}

(4, 4, 4)

Q5.
(a) Write a short note on abnormal colligative properties of solutions and van't Hoff factor.

(b) Derive thermodynamically the relation:

$$\frac{1}{T_b} = \frac{1}{T_b^*} + \frac{R \ln x_A}{\Delta H_{vap}}$$

where T_b and T_b^* are the boiling points of solution and solvent respectively and x_A is the mole fraction of the solvent.

(c) Calculate the osmotic pressure of 0.1 M solution of $K_4[Fe(CN)_6]$ at 300 K, assuming the salt to be 40% ionized in this solution.

(4, 4, 4)

Q6.

(a) Derive the relation between equilibrium constant and temperature. Comment on the result.

(b) State and explain Le-Chatelier's principle? Discuss the effect of temperature and pressure on the following reactions:

(i) $A(g) + B(g) \leftrightarrow C(s) + D(g)$ $\qquad$ $\Delta H = -x$ kJ mol^{-1}

(ii) $M(s) + N(g) \leftrightarrow X(s) + Y(s)$ $\qquad$ $\Delta H = +y$ kJ mol^{-1}

(c) The degree of dissociation of N_2O_4 is 16.7 % at 298 K and 1 atm. Calculate K_p, K_c and K_x. Also calculate standard free energy change. The dissociation process is

$N_2O_4 (g) \leftrightarrow 2NO_2 (g)$ $\qquad$ $\Delta H = 57$ kJ mol^{-1} $\qquad$ (4, 4, 4)
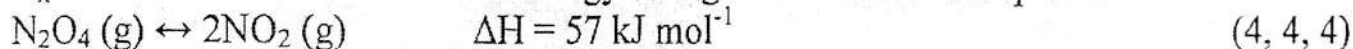
Q7.

(a) For a binary system show that

$$dv_1 = -\frac{n_2}{n_1} dv_2$$

What is the physical significance of this expression?

(b) A monobasic acid "A" has molecular weight M. The specific gravity is mentioned on the bottle of the acid "A" is Y g/cc and purity of the acid is Z% by weight. Find out the normality of the acid "A" in terms of M, Y and Z.

(c) Two ideal gases are at the same temperature but at different pressures. If n_1 moles of gas 1 and n_2 moles of gas 2 are mixed isothermally, what will be the free energy of mixing?

$\qquad$ (4, 4, 4)

Q8. Write short notes on any **three** of the following:

(a) Zeroth law of thermodynamics
(b) Exact and inexact differentials
(c) Coupled reactions
(d) Adiabatic flame temperature $\qquad$ (4 X 3)