[This question paper contains 4 printed pages]

Your Roll No. : ....2019.......

Sl. No. of Q. Paper : **7393** **J**

Unique Paper Code : 32171301

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

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

Semester : III

Time : 3 Hours *Maximum Marks : 75*

Instructions for Candidates :

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

(ii) Attempt any **five** questions.

(iii) All questions carry equal marks.

1. (a) Explain why most lines in the Ellingham diagram slope upward from left to right. What happens when a line crosses $\Delta G=0$? 5

(b) Why is white phosphorus very reactive in comparison to red phosphorus ? Give the mechanism of stepwise hydrolysis of P_4O_{10}. 5
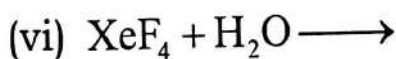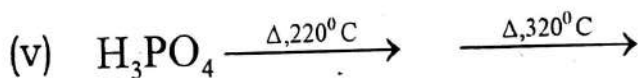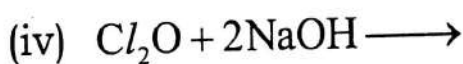
P.T.O.
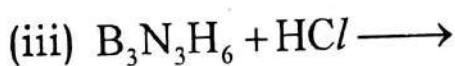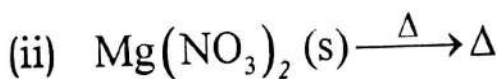
(c) How will you obtain the following : 5
  (i) B-bromoborazine from borazine
  (ii) $(NPF_2)_3$ from $(NPCl_2)_3$

2. (a) Chemistry of Lithium is different from other alkali metals. Give examples in support of the statement. 5

   (b) What are clathrate compounds of noble gases ? Why do helium and neon not form clathrates ? 5

   (c) Give one method of preparation of peroxodisulphuric acid. What is the oxidation state of Sulphur in it ? Give one reaction in support of its strong oxidizing nature. 5

3. (a) Name the class of silicates present in the following minerals. Write the basic silicate unit present in them and give their structure 5
   (i) Zircon
   (ii) Emerald or Beryl.

   (b) Among the alkaline earth metals (except Beryllium), which will (a) have the most insoluble sulfate; (b) be the softest metal. Give reason. 5

(c) Discuss the structure and bonding in Diborane. What are the products formed when diborane reacts with excess ammonia at 5
  (i) low temperature
  (ii) high temperature

4. Give reason (**any five**) : 3×5=15

   (i) P_4 molecule is more stable than the P_2 molecule.

   (ii) Ionization energy decreases from B to Al but increases from Al to Ga.

   (iii) H_2O a liquid but H_2S a gas at room temperature.

   (iv) Only the alkali metals form solid, stable hydrogen carbonate salts.

   (v) The bond angle in NH_3 is $107°$ while in PH_3 is $93°$.

   (vi) Interhalogens are more reactive than the halogens.

5. (a) Explain briefly the complex formation tendency of the alkali metals with special reference to crown ethers and cryptands. 5

   (b) (i) What are pseudohalogen compounds ? 2.5

(ii) Draw the structure of the following compounds :   2.5

ICl_3, H_2SO_5, Basic Beryllium acetate

(c) Complete the following (any **five**) :   5

(i) $CsICl_2 \xrightarrow{\Delta}$

(ii) $Mg(NO_3)_2 (s) \xrightarrow{\Delta} \Delta$

(iii) $B_3N_3H_6 + HCl \longrightarrow$

(iv) $Cl_2O + 2NaOH \longrightarrow$

(v) $H_3PO_4 \xrightarrow{\Delta, 220^0 C} \xrightarrow{\Delta, 320^0 C}$

(vi) $XeF_4 + H_2O \longrightarrow$

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

(a) Allotropes of Carbon

(b) Hydrometallurgy

(c) Inert pair effect

(d) Craig and Paddock model for imperfect delocalization of π-electrons in $(NPCl_2)_3$.

(19)

[This question paper contains 4 printed pages]

Your Roll No. : .....20.19.....

Sl. No. of Q. Paper : **7394**   **J**

Unique Paper Code : 32171302

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

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

Semester : III

Time : 3 Hours   Maximum Marks : 75

Instructions for Candidates :

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

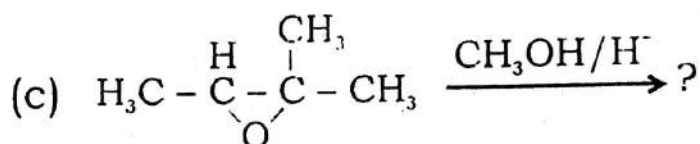(b) Attempt any **five** questions.

(c) **All** questions carry equal marks.

1. (a) An organic compound A ($C_9H_{10}O$) reacts with iodine and aq. Sodium hydroxide to give iodoform and sodium salt of an acid B ($C_8H_8O_2$). B on reaction with chlorine and red phosphorous forms compound C ($C_8H_7O_2Cl$). Hydrolysis of C followed by acidification gives compound D. Identify A, B, C, & D with the reactions involved. Name the reaction by which B is converted to C. Write the mechanism for conversion of A to B.   10

P.T.O.

(b) Write one test along with reaction involved for distinction between the following pairs of compounds :   2.5×2=5

(i) 1-Pentanol and 2-pentanol

(ii) Acetaldehyde and benzaldehyde

2. How will you prepare the compounds a, b, & c from ethyl acetoacetate and d & e from diethyl malonate ?   3×5=15

(a) 3-Methylpentan-2-one

(b) Succinic acid

(c) 2-Methylhexanoic acid

(d) Cinnamic acid

(e) 5-Ethylbarbituric acid

3. Explain the following :   3×5=15

(a) The rate of hydrolysis of the carboxylic acid derivatives is

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

(b) S_N1 reactions are accompanied by racemization as well as inversion of configuration.

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

(d) Reactivity of aryl halidas towards nucleophilic substitution increases with the substitution of nitro group at *ortho*-and *para*-positions.

2

(e) t-Butyl methyl ether is prepared by reaction of methyl chloride and sodium t-butoxide rather than from t-butyl chloride and sodium methoxide.

4. Write the products for the following along with equations :   3×5=15

(a) When oxalic acid, succinic acid and adipic acid are heated separately.

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

(c) Phenol is heated with carbon dioxide under presure in the presence of sodium hydroxide followed by reaction with acetic anhydride in the presence of acid catalyst.

(d) Acetone when reacted with hydroxy*l* amine followed by treatment with Conc. H_2SO_4.

(e) Maleic acid and fumaric acid are treated separately with dil. $KMnO_4$.

5. How will you carry out the following conversions ?   3×5=15

(a) Ethanoic acid to Propanoic acid

(b) Benzene to ethoxybenzene

(c) Acetone to 2-methyl-2-butanol

(d) Benzaldehyde to benzamide

(e) Aniline to fluorobenzene

6. Complete the following reactions. Write the mechanism of the reaction involved. $5 \times 3 = 15$

(a) $CH_3CH_2CHO \xrightarrow{\text{Dil. NaOH}} ?$

(b) $C_6H_5CHO \xrightarrow{\text{Aq. Alc. KCN}} ?$

(c) $H_3C - \underset{\underset{O}{\diagdown\diagup}}{\overset{\overset{H}{|}}{C}} - \underset{\overset{|}{CH_3}}{\overset{CH_3}{C}} - CH_3 \xrightarrow{CH_3OH/H^-} ?$
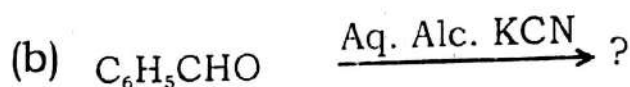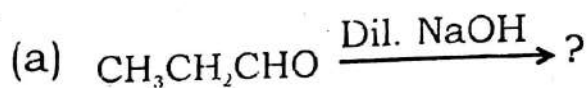
7. Write short notes on any **three** of the following with emphasis to (i) the functional group that undergoes these reactions, (ii) products formed, (iii) reaction conditions and (iv) mechanism.

$5 \times 3 = 15$

(a) Baeyer-Villiger oxidation

(b) Cannizzaro reaction

(c) Fries rearrangement

(d) Benxil-benzilic acid rearrangement

(e) Michael addition

[This question paper contains 7 printed pages]

Your Roll No. : ...2019....

Sl. No. of Q. Paper : **7395** **J**

Unique Paper Code : 32171303

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

Name of the Paper : Physical Chemistry - III :
Phase Equilbria and
Electrochemical Cells

Semester : III

Time : 3 Hours **Maximum Marks : 75**

Instructions for Candidates :

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

(ii) Question No. **1** is compulsory.

(iii) Attempt **six** questions in all, selecting at
least **two** questions from each Section.

(iv) Use of scientific calculator is allowed.

Values of constants :

$R = 8.314$ J K^{-1} mol^{-1},

$F = 96500$ C mol^{-1}, (2.303 RT/F) at 298 K = 0.0591

P.T.O.

1. Explain (any **five**) :   3×5=15

   (a) How can liquid junction potential be eliminated ?

   (b) Quinhydrone electrode is not suitable for pH measurement more than 8.5.

   (c) Difference between electrolytic and galvanic cell.

   (d) Use of adsorbent in powdered form.

   (e) Slope of fusion curve of water system is inclined towards pressure axis.

   (f) Plait point lies either to the left or right of the maximum of the binodal curve in a three component system.

   (g) Triethylamine-water system shows lower CST.

   ## Section - A

2. (a) Derive phase rule for a non-reactive system.
                                                          4

   (b) Show that $NH_4Cl(s) - NH_3(g) - HCl(g)$ system in which $P_{NH3}=P_{HCl}$ is a one component system whereas when $P_{NH3} \neq P_{HCl}$ is a two component system.   4

   (c) The vapour pressure of toluene is 59.1 torr at 313.75K and 298.7 torr at 353.15K. Calculate the molar heat of vaporization.
                                                          4

3. (a) Differentiate between congruent and incongruent melting point system with an example.   4

   (b) Metal A and B melts at 110°C and 75°C respectively. They form one compound A_2B which decomposes at 20°C to give a solid and a melt containing 50mole % of B. There is a eutectic point at 5°C and eutectic composition is 70 mole % of B. Sketch the phase diagram and label it.   4

   (c) Show that multistage extraction is more economical than single stage extraction.
                                                          4

4. (a) Derive Duhem Margules equation as applicable to a binary liquid mixture and show that if one component behaves ideally then other component also behaves ideally.

4

(b) Calculate the degree of freedom at a point which lies any where :

4

   (i) Outside the binodal curve

   (ii) Within the binodal curve

(c) Write a short note on fractional distillation.

4

5. (a) State and derive the lever rule. 4

(b) Draw a well labelled phase diagram of choloroform-acetic acid- water system.

4

(c) The vapour pressure of aniline and water at 98.5°C are 717mm and 43mm respectively. Molar masses of liquids are 93 and 18. Calculate the relative masses of two liquids in the distillate after the steam distillation.

4

Section - B

6. (a) How will you determine the accurate value of half-cell potential graphically ? 4

(b) For the following cell : 4

$Pb \mid PbCl_2(s) \mid PbCl_2(sol^n) \mid AgCl(s) \mid Ag.$
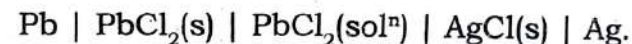
The potential at 298K is 0.490V and the variation of emf with temperature is given by :

$E= a-(1.86 \times 10^{-4}VK^{-1})(T - 25K)$

Calculate ΔG, ΔH and ΔS for the reaction at 298 K.

(c) Describe the construction of hydrogen electrode along with necessary diagram and chemical equations. Give its limitation also.

4

7. (a) What are concentration cells ? Derive the expression for a concentration cell with transference. 4

(b) Calculate the cell potential at 25°C for the cell : 4

$Pt \mid H_2(p =1 \, bar) \mid HBr(a \pm =0.2) \mid Hg_2Br_2(s) \mid Hg$

Given $E^0_{Br- \mid Hg2Br2 \mid Hg}=0.1385V$
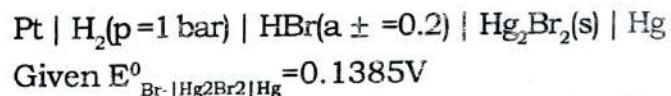
(c) Construct the galvanic cell for the following reactions and write the expression for the cell potential 4

   (i) $Zn(s)+H_2SO_4(aq) \rightarrow ZnSO_4(aq)+H_2(g)$

   (ii) $Ag^+(aq)+Cl^- (aq) \rightarrow AgCl (s)$
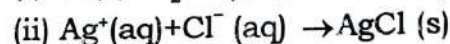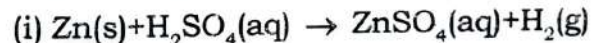
8. (a) Explain :   4

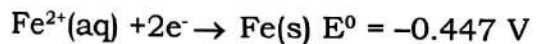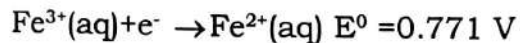   (i) Why chemisorption is monolayer and physiosorption is multilayer.

    (ii) Most adsorption process are exothermic in nature.

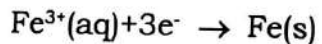(b) Derive the following Langmuir Adsorption isotherm :   4

$$\frac{p}{x/m} = \frac{1}{k1k2} + \frac{p}{k2}$$

Explain the various symbols.

(c) From the following reduction reactions and E^0 values :   4

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^0 = 0.771$ V

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^0 = -0.447$ V

Calculate E^0 for the half-cell reaction

$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$

$4 \times 3 = 12$

9. Write short note (any **three**) :

    (i) Potentiometric titrations

    (ii) Reversible and irreversible galvanic cells

    (iii) Different types of half cells

    (iv) Glass electrode

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

Semester : III

Name of the Paper: Inorganic Chemistry-II

Unique Paper Code: 217301

Old Code: CHHT-305

Attempt any five questions. Each question carries 15 marks.

Q1 a) Derive Born Lande's equation for calculating lattice energy of ionic crystals. Explain the various terms involved.

b) Which will have higher lattice energy; NaCl or CsCl and why? (both have the same crystal structures)

c) Draw Born Haber's Cycle for formation of NaCl.

d) Why is doping done in semiconductors?   (5,3,4,3)

Q2 a) Discus , why B_2 is paramagnetic and C_2 is diamagnetic using M.O. theory. (4,3,3, 5)

b) Compare valence bond theory and molecular orbital theory.

c) Which is more ionic PbO_2 or PbO? Why?

d) Bond distance in HF is 0.917×10^{-10} m. Find the % ionic character given that the observed dipole moment of the molecule is 6.6×10^{-30} coloumb meter.)e $= 1.602 \times 10^{-19}$ C)

Q3 a) PCl_3 is a lewis base and not a lewis acid while PCl_5 is a lewis acid and not a lewis base.

b) Using VSEPR theory, predict the geometry of: SO_4^{2-}, SF_4, XeO_2F_2, ClF_3, CO_3^{2-}

c) BF_4^- is tetrahedral while BrF_4^- is planer. Explain.   (5,5,5)

Q4 a) Explain the order of decreasing basicity for methylamine, pyridine and methylcyanide.

b) Does Urea behave as a base or acid in water? What will be its behavior in liquid ammonia?

c) Give the increasing order of the acidic strength giving reasons:
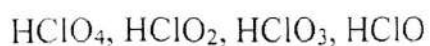
$HClO_4$, $HClO_2$, $HClO_3$, $HClO$ (5,5,5)

Q5 a) What is Bent's rule? Using the rule explain which is more stable PCl_3F_2 or PCl_2F_3.

b) Explain HSAB principle and what are its applications?

c) Distinguish between: i) ionic and covalent bond

ii) Equivalent and on-equivalent hybrid orbitals (5,5,5)

Q6 a) What is hydrogen bonding? Explain the different types of hydrogen bonds and give suitable examples.

b) The bond angle of NH_3 > NF_3 while the bond angle of PF_3 > PH_3. Explain.

c) Calculate the lattice energy of MgO (in KJ/mol). Given A = 1.7475, r (Mg^{2+}) = 0.65 Å, r (O^{2-}) = 1.40 Å, n=7, e= 4.8X 10^{-10} esu. (5,5,5)

(5,5,5)

Q7 Write short notes on:

i) Resonance and resonance energy
ii) Solvation energy
iii) Stoichiometric defects.

SI-No. 7)   Q.P : 8845

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Your Roll No. 2019

Unique Paper Code   : 217303

Name of the Paper   : 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 **Six** questions in all.
3. Question no.1 is **compulsory** and carries **15** marks.
4. All other questions are of **12 marks** each.

1. An organic compound **A** having molecular formula $C_9H_{10}O$ reacts with NH_2OH to give two isomers **B** and **C** with molecular formula $C_9H_{11}ON$. The compounds **B** and **C** on treatment with PCl_5 isomerizes to compound **D** and **E**. Compound **F** having molecular formula $C_8H_8O_2$ may be formed either from **A** by the action of KIO_3 or from **D** by hydrolysis. Hydrolysis of **E** gives *o*-toluidine. Identify **A** to **F** and give the reactions involved.   (15)

2. (a) How will you distinguish between 1°, 2° and 3° alcohols?

   (b) Why is phenol more acidic than alcohols? Explain by giving resonance structures.

   (c) *o*-Chloroanisole and *m*-chloroanisole gives the same product with $NaNH_2$ and liq. NH_3. Explain with mechanism.

   (d) Why is benzyl chloride more reactive than ethyl chloride towards nucleophilic substitution reaction?   (3,3,3,3)

3. (a) How will you synthesize Phenol from Cumene?

   (b) Differentiate between SN_1 and SN_2 reactions.

   (c) Which among the following is the most reactive towards nucleophilic acyl substitution reactions. Give reasons for your answer.
   $RCOCl$, $RCOOR$, $RCONH_2$ (4,4,4)

4. (a) What is the effect of heat on α, β and γ-hydroxy acids?

(b) Why is o-nitrophenol weaker acid than p-nitrophenol?

(c) How will you prepare 2-methylpropan-2-ol using Grignard reagent?

(d) Acid derivatives do not form 2,4-dinitrophenylhydrazone though they have carbonyl group. Explain. (3,3,3,3)

5. (a) How will you distinguish between the following pairs of compounds? Write one method with the reaction(s) involved:
  (i) Phenol and Ethanol
  (ii) Acetaldehyde and Acetone
  (iii) Acetophenone and Benzaldehyde
  (iv) Benzoic acid and Phthalic acid

(b) What is the role of CN^- ion during Benzoin condensation? (8,4)

6. (a) How will you prepare the following compounds from ethyl acetoacetate or diethyl malonate? (Any **three**)
  (i) Cinnamic acid
  (ii) 5-Ethyl barbituric acid
  (iii) Succinic acid
  (iv) Acetone

(b) How will you convert benzaldehyde to benzamide? (9,3)

7. Write short notes on any three of the following:
  (a) Reimer-Tiemann reaction
  (b) Friedel's Crafts reaction
  (c) Wittig reaction
  (d) Aldol Condensation
  (e) Pinacol-Pinacolone rearrangement (4,4,4)

(23)

Unique Paper Code   : 217305

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

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.

3. Q. No. 1 is compulsory.

    Given

    $R = 8.314 \ J \ K^{-1} mol^{-1}$; $N_A = 6.022 \times 10^{23} \ mol^{-1}$

                                                                    $5 \times 3 = 15$

1. Attempt *any five* of the following:

(a) What is the difference between bond enthalpy and bond dissociation enthalpy?

(b) The magnitude of the boiling point elevation is less than that of the freezing point depression. Explain

(c) Explain Hess's Law of constant heat summation with an example.

(d) The residual entropy of O_2 is zero, but that of CO is not zero at absolute zero. Why?

(e) Why is the value of C_p always greater than C_v?

(f) Explain why, for mixing of two solvents to form an ideal solution, $\Delta V_{mix} = 0$?

(g) What is Le Chatelier's principle?

                                                                    $4 \times 3 = 12$

2. Derive the following:

(a) $TV^{\gamma-1} = $ Constant

(b) $\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$

(c) $\left(\dfrac{\partial(\Delta G/T)}{\partial(1/T)}\right)_P = \Delta H$

3.
(a) The Joule- Thompson coefficient of a gas can be positive, negative or zero. Comment.

(b) The bond enthalpy of $H_2(g)$ is 436 kJ mol^{-1} and that of $N_2(g)$ is 941.3 kJ mol^{-1}. Calculate the average bond enthalpy of an N-H bond in ammonia. $\Delta H_f^0(NH_3) = -40.0$ kJ mol^{-1}.

(c) What are exact and inexact differentials? Show that 'dw' is an inexact differential

4×3=12

4.
(a) Write a short note on abnormal colligative properties of solutions and van't Hoff factor.

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

4×3=12

(c) Derive

$$\Delta T_f = \dfrac{RT_0^2 M_1}{\Delta H_{fus}} \times m$$

5.
(a) State and explain the Zeroth law of thermodynamics. Also discuss its applications.

(b) What are intensive and extensive properties? Is internal energy is extensive or intensive property?

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

4×3=12

6.
(a) Explain, while the equilibrium constant K_p of a gaseous reaction is independent of pressure, K_x is not.

(b) At a total pressure of 2 atmospheres and 673K the equilibrium constant Kp for the following reaction is 1.64×10^{-4}. Calculate K_c and K_x.

$$N_2O_4(g) \Leftrightarrow 2NO_2(g)$$
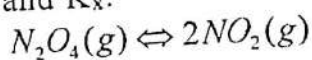
(c) Derive the expression $\Delta G^0 = -RT\ln K_p$ for a reaction in equilibrium using concept of Gibbs free energy.

4×3=12

4×3=12

7.
(a) An ideal solution is made from mixing 5.0 mol of Benzene and 3.25 mol of Toluene. Calculate ΔG_{mixing} and ΔS_{mixing} at 25°C and 1 atm pressure. Is mixing a spontaneous process ? Justify your answer.

(b) For the dissociation of $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, derive the expression

$\alpha = \left(\frac{K_p}{P}\right)^{1/2}$; where α is the the degree of dissociation, K_p is the equilibrium constant and P is the total pressure.

(c) Derive additivity rule for chemical potential.

4×3=12

8. Write short notes on *any three* of the following:
(a) Trouton's rule
(b) Second law of thermodynamics
(c) Intergral enthalpy of solution
(d) Raoult's law of ideal solutions