1. (a) Explain why most lines in the Ellingham diagram slope upward from left to right. What happens when a line crosses ΔG=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
2. (a) Chemistry of Lithium is different from other alkali metals. Give examples in support of the statement.
(b) What are clathrate compounds of noble gases? Why do helium and neon not form clathrates?
(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.

3. (a) Name the class of silicates present in the following minerals. Write the basic silicate unit present in them and give their structure.
(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.

4. Give reason (any five):
(i) P₄ molecule is more stable than the P₂ molecule.
(ii) Ionization energy decreases from B to Al but increases from Al to Ga.
(iii) H₂O a liquid but H₂S a gas at room temperature.
(iv) Only the alkali metals form solid, stable hydrogen carbonate salts.
(v) The bond angle in NH₃ is 107° while in PH₃ 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.
(b) (i) What are pseudohalogen compounds?
(ii) Draw the structure of the following compounds:
ICI₃, H₂SO₅, Basic Beryllium acetate

(c) Complete the following (any five):

(i) CsICl₂ $\xrightarrow{\Delta}$

(ii) Mg(NO₃)₂(s) $\xrightarrow{\Delta}$Δ

(iii) B₃N₃H₆ + HCl $\rightarrow$

(iv) Cl₂O + 2NaOH $\rightarrow$

(v) H₃PO₄ $\xrightarrow{\Delta,220^\circ C}$ Δ,$\xrightarrow{\Delta,320^\circ C}$

(vi) XeF₄ + H₂O $\rightarrow$

6. Write short notes on (any three):

(a) Allotropes of Carbon
(b) Hydrometallurgy
(c) Inert pair effect
(d) Craig and Paddock model for imperfect delocalization of π-electrons in (NPCl₂)₃.
1. (a) An organic compound A (C₉H₁₀O) reacts with iodine and aq. Sodium hydroxide to give iodoform and sodium salt of an acid B (C₆H₈O₂). B on reaction with chlorine and red phosphorous forms compound C (C₈H₇O₂Cl). 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
(b) Write one test along with reaction involved for distinction between the following pairs of compounds:

(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?

(a) 3-Methylpentan-2-one
(b) Succinic acid
(c) 2-Methylhexanoic acid
(d) Cinnamic acid
(e) 5-Ethylbarbituric acid

3. Explain the following:

(a) The rate of hydrolysis of the carboxylic acid derivatives is
   \[ \text{CH}_3\text{COCl} > (\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{CONH}_2. \]
(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 halides towards nucleophilic substitution increases with the substitution of nitro group at ortho- and para-positions.

(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:

(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 pressure in the presence of sodium hydroxide followed by reaction with acetic anhydride in the presence of acid catalyst.
(d) Acetone when reacted with hydroxyl 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?

(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

P.T.O.
6. Complete the following reactions. Write the mechanism of the reaction involved.  \( 5 \times 3 = 15 \)

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

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

(c) \( \ce{H_3C-C-C-CH_3} \xrightarrow{\text{CH_3OH/H^+}} ? \)

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
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 Equilibria 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):

(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.

(b) Show that $\text{NH}_4\text{Cl}(s) - \text{NH}_3\text{ (g)} - \text{HCl(g)}$ system in which $P_{\text{NH}_3} = P_{\text{HCl}}$ is a one component system whereas when $P_{\text{NH}_3} \neq P_{\text{HCl}}$ is a two component system.

(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.

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

(b) Metal A and B melts at 110°C and 75°C respectively. They form one compound $A_B$ which decomposes at 20°C to give a solid and a melt containing 50 mole % 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.

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

(b) Calculate the degree of freedom at a point which lies anywhere:
   (i) Outside the binodal curve
   (ii) Within the binodal curve

(c) Write a short note on fractional distillation.

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

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

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

Section - B

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

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

(b) Calculate the cell potential at 25°C for the cell:
   \[ \text{Pt} | \text{H}_2(p=1 \text{ bar}) | \text{HBr(aq)}(a=0.2) | \text{Hg}_2\text{Br}_2(s) | \text{Hg} \]
   Given \( E^\circ_{\text{Br}^-|\text{Hg}_2\text{Br}_2|\text{Hg}} = 0.1385 \text{V} \)

(c) Construct the galvanic cell for the following reactions and write the expression for the cell potential
   (i) \( \text{Zn(s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{H}_2(g) \)
   (ii) \( \text{Ag}^+(aq) + \text{Cl}^- (aq) \rightarrow \text{AgCl (s)} \)
8. (a) Explain:

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

(ii) Most adsorption processes are exothermic in nature.

(b) Derive the following Langmuir Adsorption isotherm:

\[
\frac{p}{x/m} = \frac{1}{k_1} + \frac{p}{k_2}
\]

Explain the various symbols.

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

\[
\begin{align*}
Fe^{3+}(aq) + e^- &\rightarrow Fe^{2+}(aq) \quad E^0 = 0.771 \, V \\
Fe^{2+}(aq) + 2e^- &\rightarrow Fe(s) \quad E^0 = -0.447 \, V
\end{align*}
\]

Calculate \( E^0 \) for the half-cell reaction

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

9. Write short note (any three):

(i) Potentiometric titrations
(ii) Reversible and irreversible galvanic cells
(iii) Different types of half cells
(iv) Glass electrode

4 \times 3 = 12
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) Discuss why B₂ is paramagnetic and C₂ is diamagnetic using M.O. theory. (4,3,3,5)
   b) Compare valence bond theory and molecular orbital theory.
   c) Which is more ionic PbO₂ or PbO? Why?
   d) Bond distance in HF is 0.917X10⁻¹⁰ m. Find the % ionic character given that the observed dipole moment of the molecule is 6.6X10⁻³⁰ coulomb meter. \( \mu = 1.602 \times 10^{-19} \text{ C} \)

Q3  a) PCl₃ is a lewis base and not a lewis acid while PCl₅ is a lewis acid and not a lewis base.
   b) Using VSEPR theory, predict the geometry of: SO₄²⁻, SF₄, XeO₂F₂, ClF₃, CO₃²⁻
   c) BF₄⁻ is tetrahedral while BrF₄⁻ is planar. Explain. (5,5,5)

Q4  a) Explain the order of decreasing basicity for methyamine, 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:
a) What is Bent's rule? Using the rule explain which is more stable PCl_{3}F_{2} or PCl_{2}F_{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

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 \, \text{Å}, r (O^{2-}) = 1.40 \, \text{Å}, n=7, e= 4.8 \times 10^{-10} \text{ esu}.

Q7 Write short notes on:

i) Resonance and resonance energy

ii) Solvation energy

iii) Stoichiometric defects.
1. An organic compound A having molecular formula C₉H₁₀O reacts with NH₂OH to give two isomers B and C with molecular formula C₉H₁₁ON. The compounds B and C on treatment with PCl₅ isomerizes to compound D and E. Compound F having molecular formula C₈H₈O₂ may be formed either from A by the action of KIO₃ 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 NaN₃ and liq. NH₃. 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 SN₁ and SN₂ reactions.
(c) Which among the following is the most reactive towards nucleophilic acyl substitution reactions. Give reasons for your answer.

RCOCl, RCOOR, RCONH₂ (4,4,4)
4. (a) What is the effect of heat on α, β and γ-hydroxy acids?

(b) Why is α-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.

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?

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?

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
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

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

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?

2. Derive the following:

   (a) \( TVy^{-1} = \text{Constant} \)
The Joule-Thompson coefficient of a gas can be positive, negative or zero. Comment.

The bond enthalpy of H₂(g) is 436 kJ mol⁻¹ and that of N₂(g) is 941.3 kJ mol⁻¹. Calculate the average bond enthalpy of an N-H bond in ammonia, \( \Delta H_{f}(\text{NH₃}) = -40.0 \text{ kJ mol}^{-1} \).

What are exact and inexact differentials? Show that 'dw' is an inexact differential.

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

Calculate the osmotic pressure of 0.1 M solution of K₄[Fe(CN)₆] at 300K, assuming the salt to be 40% ionised in this solution.

\[ \Delta T_f = \frac{RT_0^2M_1}{\Delta H_{iun}} \times m \]

State and explain the Zeroth law of thermodynamics. Also discuss its applications.

What are intensive and extensive properties? Is internal energy an extensive or intensive property?

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:

\[
\begin{align*}
C_p \text{(H}_2\text{O(s), 0-273 K)} & = 30 \text{ J K}^{-1}\text{mol}^{-1} \\
C_p \text{(H}_2\text{O(l), 273-373 K)} & = 75 \text{ J K}^{-1}\text{mol}^{-1}; \Delta H_{\text{fusion}} = 65 \text{ kJ mol}^{-1} \\
C_p \text{(H}_2\text{O(v), 373-400 K)} & = 36 \text{ J K}^{-1}\text{mol}^{-1}; \Delta H_{\text{vap}} = 40 \text{ kJ mol}^{-1}
\end{align*}
\]

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

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

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g) \]

\[ \Delta G^0 = -RT\ln K_p \]

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

For the dissociation of \( \text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g) \), derive the expression...
\[ \alpha = \left( \frac{K_p}{p} \right)^{1/2} \]; where \( \alpha \) is the degree of dissociation, \( K_p \) is the equilibrium constant and \( p \) is the total pressure.

(c) Derive additivity rule for chemical potential.

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