(1)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 4306          G

Unique Paper Code          : 32171102

Name of the Paper          : Physical Chemistry I: States of Matter & Ionic Equilibrium

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

Semester                   : I

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. Answer any **six** questions.

3. Use of calculator is allowed.

1. Explain briefly :

   (a) Water does not spread over the surface of oil.

(2)

P.T.O.

(b) Insects move on the surface of the water without sinking. (2)

(c) What are the forces which are responsible for the viscosity of a liquid? Why is glycerol more viscous than water? (2)

(d) Why are the X rays used as the source beam? (2)

(e) What is Unit Cell? (2)

(f) The hydrolysis constant for $ZnCl_2$ is $K_w^2/K_b$. (2.5)

2. (a) Define coefficient of viscosity of liquid, give its S.I. units. Describe a method for its experimental determination.

(b) If the number of drops for the two liquids A and B through the same capillary is in the ratio of 1:2 and the densities in the ratio of 2:3. What is the ratio of their surface tensions?

(c) Calculate the pH of a solution obtained by dissolving $5 \times 10^{-4}$ moles of Ca $(OH)_2$ to 1 L of solution at 298 K. (4,4,4,5)

3. (a) Evaluate the Miller Indices for the planes with the following intercepts :

      (i) 0a, 2b, 3c

      (ii) 2a, 3c, ~3b

      (iii) a, 1/6 b, 1/3c

      (iv) a, 2b, c

(b) What do you mean by element of symmetry of a crystal? Explain with one example.

(c) Calculate the number of atoms contained within a primitive cubic unit cell, a body centred cubic unit cell and a face centred cubic unit cell. (4,4,4,5)

P.T.O.

4. (a) Calculate the pH of a solution obtained by mixing 25 mL of 0.2 M HCl with 50 mL of 0.25 M NaOH.

(b) Write the expression for rms speed, average speed and most probable speed of a gas molecule. What will be the pH of a solution obtained by mixing 5 g of acetic acid and 7.5 g of sodium acetate and making a volume of 500 mL, pKa = 4.76.

(c) What is salt hydrolysis? Calculate the degree of hydrolysis of 0.10 M solution of sodium acetate at 25°C. $K_a = 1.75 \times 10^{-5}$, $K_w = 10^{-14}$. (4,4,4.5)

5. (a) Write short notes on :

(i) The most probable velocity,

(ii) The average velocity

(iii) Root mean square velocity.

(b) What is critical compressibility factor? Calculate the critical temperature of a van der Waal's gas for which $P_c$ is 100 atm and 'b' is 50 cm³/mol.

(c) What is solubility product? Discuss its various applications. (4,4,4.5)

6. (a) $10^{-2}$ mol of NaOH was added to 10 litres of water. What will be the pH of the solution?

(b) What is the reason for Brownian motion? List the factors affecting the mean free path.

(c) Write short note on any two: collision number, collision frequency collision diameter and mean free path. (4,4,4.5)

7. (a) Give reason of the following :

      (i) Why phenolphthalein is not suitable indicator for titrating a weak base against a strong acid?

      (ii) Why methyl orange cannot be used as indicator for titrating a weak acid, against a strong base?

(b) What is interfacial tension? What are surface active agents? How these agents affects surface tension?

(c) What type of interaction holds the molecules together in polar molecular solid? What are miller indices? Write the intercepts if the miller indices are (1, 2, –2).                          (4,4,4.5)

8. (a) How would you differentiate between crystalline and amorphous solids?

(b) What are Boyle's, Charles's and Avogadro's law? Explain with the help of graphs.

(c) Salt of strong acid and Base do not hydrolyse. Why? Calculate the percentage hydrolysis of sodium acetate in 0.1M solution at 25°C assuming that the salt is completely dissociated. $K_a$ of acetic acid is $1.75 \times 10^{-5}$. Ionic product of water is $10^{-14}$. (4,4,4.5)

9. (a) What is compressibility factor? How is it affected by charge in pressure and temperature in different gases?

(b) How does the viscosity of a liquid and gas varies with temperature?

(c) What is Buffer index? A buffer solution contains 0.20 mol of $NH_4OH$ and 0.5 mol of $NH_4Cl$ per litre. Calculate the pH of the solution. Dissociation Constant of $NH_4OH$ at room temperature is $1.81 \times 10^{-5}$.                                    (4,4,4.5)

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

Sr. No. of Question Paper : 4342          G

Unique Paper Code          : 32171301

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

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

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. Question No. **1** is compulsory.

3.  **All** Questions carry equal marks.

1.  Explain the following giving reasons : **(any five)**

    (a) $CCl_4$ does not act as a Lewis acid while $SiCl_4$ does.

P.T.O.

(b) Borazine is more reactive than Benzene.

(c) Amongst the alkali metals Lithium has got the highest ionisation enthalpy, despite this it is as good a reducing agent as cesium in aqueous solution.

(d) Carbon is a versatile reducing agent used in the extraction of metals, but it is unsuitable sometimes as a reducing agent.

(e) Phosphorus, arsenic and antimony form pentahalides, but nitrogen and bismuth do not.

(f) $B^{3+}$ ion doesn't exist in solid or solution state.

(g) Zeolites are used as water softeners.       (3×5)

2.   (a) Select the correct answer in each category given below and justify your answer. **(any four)**

(i) A halogen which does not exhibit positive oxidation state: Flourine or chlorine

(ii) Better lewis base: Trimethylamine or trisilylamine

(iii) Stronger reducing agent: $CH_4$ or $SiH_4$

(iv) Hydride having higher thermal stability: $NH_3$ or $PH_3$

(v) Stronger oxidising agent: $HOCl$ or $HClO_4$

(b) Explain with the help of Ellingham diagram, the reducing nature of carbon and carbon monoxide.

(c) Graphite is soft, has low density and is a good conductor of electricity but diamond is extremely hard, has high density and is a non-conductor of electricity. Explain why? (6,4,5)

3. Justify the following statements, giving reason :

(a) Methane, ammonia and water have same hybridisation but different structures.

(b) Nitrogen is an inert gas while phosphorous is a highly reactive solid.

(c) $CO_2$ is a gas while $SiO_2$ is a high melting solid.

(d) Rubidium as compared to sodium has greater electrical conductivity in aqueous solution.

(e) Dilute solution of sodium in liquid ammonia is blue coloured, paramagnetic in nature and behaves as a true solution. (3×5)

4. (a) What is Inert pair effect? How does it vary down the group 14 elements? Explain.

(b) Draw the structure of $S_8$ molecule and explain the effect of heating on Sulphur.

(c) Discuss the structures of **any two** of the following :

      (i) Phosphorous pentoxide

      (ii) Basic beryllium acetate

      (iii) Xenon hexaflouride

(d) Silicon analogues of alkene and alkyne are not known. Give reason.         (4,4,4,3)

5. (a) Which has greater bond angle and why? $NH_3$ or $NF_3$.

(b) Which will have greater ionic radius and why? Gallium or Aluminium.

(c) A group 2 metal (M) occurs naturally in great abundance as carbonate. Metal (M) reacts with cold water forming compound (A), which is a strong base. Aqueous solution of (A) is used in the qualitative test for carbonate ion. Metal (M) combines with $H_2$ to give a saline hydride (B), which behaves as a drying agent. Identify (M), (A) and (B) giving balanced chemical reactions.

(d) Write short notes on **any two** of the following :

(i) van Arkel de Boer Method

(ii) Clathrate compounds

(iii) Phosphonitrilic halides          (3,3,3,6)

6.    (a) Potassium permanganate which is insoluble in benzene, dissolves readily in it in the presence of 18-crown-6-ether. Explain giving reason.

(b) Which is oxidising in nature and why? PbO or PbO$_2$

(c) Discuss the structure of XeF$_2$ using Molecular orbital theory.

(d) Justify the statement: Unlike ethane, diborane is an electron deficient compound. How do you explain the structure of diborane then?

(e) Write balanced chemical reactions for **any three** of the following :

   (i) Diborane reacts with ammonia in the ratio 1:2 at 200°C.

   (ii) Borazine reacts with methanol.

   (iii) Sulpur dioxide reacts with acidified solution of potassium dichromate.

(iv) Lithium nitrate is heated.

(3×5)

(1000)

Sr. No. of Question Paper : **4396**          **G**

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 any **five** questions.

1.  (a) An organic compound **A** ($C_4H_8O$) reacts with
        hydroxylamine in the presence of an acid to
        give two isomeric compounds **B** and **C** with
        molecular formula ($C_4H_9NO$). **B** reacts with *m*-

P.T.O.

chloroperbenzoic acid and gives organic compound D ($C_4H_9NO$). D on hydrolysis gives acetic acid and ethanamine. C reacts with *m*-chloroperbenzoic acid to give organic compound E ($C_4H_9NO$). E on hydrolysis gives propanoic acid and methanamine. Identify the organic compounds **A, B, C, D** and **E**. Give the name reaction involved along with mechanism (**B to D**).

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

    (i) Methanol and ethanol

    (ii) Benzoic acid and benzyl alcohol

    (iii) Benzaldehyde and propanal

    (iv) Formic acid and benzoic acid       (9,6)

2. (a) Identify organic compound A ($C_4H_{10}O_2$) which reacts with sodium metal to evolve one mole of hydrogen gas and on reaction with lead tetraacetate gives methanal and propanal. Write down the structure of the organic compound A ($C_4H_{10}O_2$) along with both the reactions involved.

(b) What happens when malonic acid, succinic acid and adipic acid are heated at 200°C separately?

(c) Why o-bromoanisole and m-bromoanisole give the same product on reaction with $NaNH_2$ in $NH_3$ (l) at high temperature? Explain giving mechanism.

(d) Identify A and B and justify your answer with the help of mechanism :
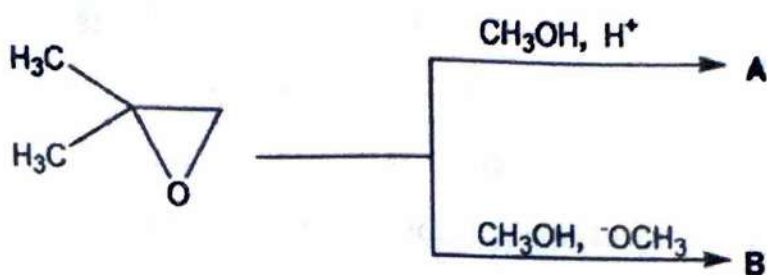


(3,3,3,6)

3.  (a) Give reasons for the following (any four) :

    (i) In the Reformatsky reaction, magnesium should not be used in place of zinc.

    (ii) During the reaction of carbonyl compounds with ammonia derivatives, pH of the reaction should be well controlled.

(iii) $-R$ group at $o$, $p$-position in aryl halide facilitates $Ar_NS$ (Aryl nucleophilic substitution) reaction.

(iv) $p$-Dimethylaminobenzaldehyde does not respond to Cannizzaro's reaction.

(v) Aryl vinyl ethers readily undergo hydrolysis in acidic medium to give phenol.

(vi) Polar protic solvents speed up an $S_N1$ reaction enormously, while it slows down $S_N2$ reaction by a factor as large as $10^{20}$.

(b) Hydrolysis of an ester is preferred in alkaline medium. Explain.

### OR

Write down the products of the following reaction and give explanation for your answer.
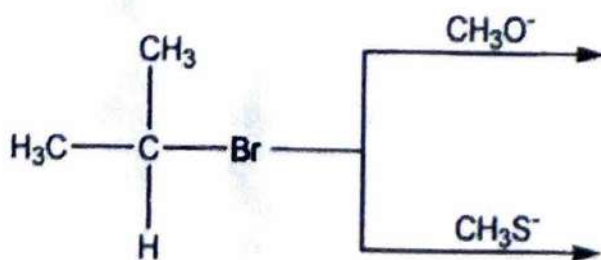


(3,3,3,3,3)

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

    (i) Toluene → Cinnamic acid

    (ii) Ethanal → Butanol

    (iii) Benzene → 1-Phenylpropane

    (iv) Benzoic acid → Acetophenone

    (b) Write down the product(s), name and mechanism of the following reaction :
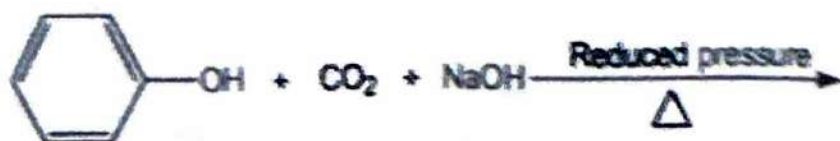


    Why *ortho* product is the major product in the above reaction?                          (3,3,3,6)

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

    (i) Succinic acid

    (ii) Pentan-2-one

(iii) Barbituric acid (Malonyl urea)

(iv) Hexane-2,5-dione

(b) Arrange the following compounds in decreasing order of reactivity towards nucleophilic substitution reaction with suitable explanation :
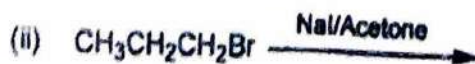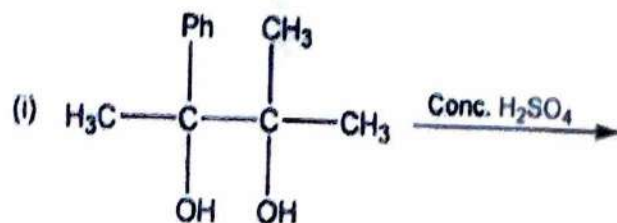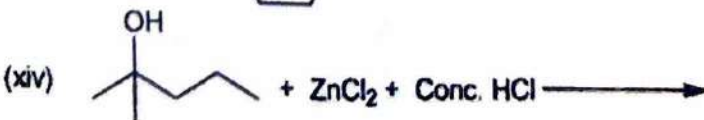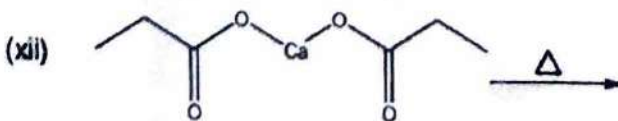


(i) CH₃CH₂Br   (ii) C₆H₅—Br   (iii) CH₂=CH—CH₂—Br
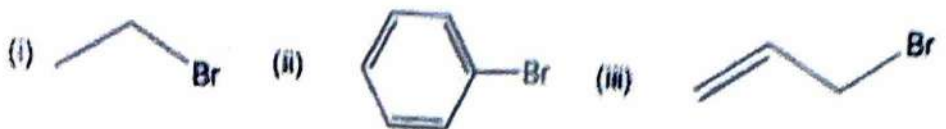
**OR**

Explain why benzyne have a shorter life-time.

(c) Why enol form of acetylacetone is more stable than that of acetone. (3,3,3,3,3)

6. Complete the following reactions : (15)



$$ \text{(i)} \quad H_3C-\underset{\underset{OH}{|}}{\overset{\overset{Ph}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4} $$

(ii) $CH_3CH_2CH_2Br \xrightarrow{\text{NaI/Acetone}}$

(iii) C₆H₅—CHO + (CH₃CO)₂O $\xrightarrow[\Delta]{CH_3COO^-Na^+}$

(iv) C₆H₅—OH + C₆H₅—COCl $\xrightarrow{10\% NaOH}$

(v) C₆H₅—OH + CHCl₃ + NaOH $\xrightarrow{60°C}$

(vi) $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$ $\xrightarrow[\Delta]{P_2O_5}$

(vii) C₆H₅—OH $\xrightarrow[(Pyridine)]{(CH_3)_2SO_4}$

(viii) Ph-CH₂-CH₂-COOEt $\xrightarrow{LAH}$

(ix) $H_3C-$C₆H₄$-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ $\xrightarrow[(ii)\ HCl]{(i)\ Anhydrous\ AlCl_3}$

(x) $2\ \underset{COOH}{\overset{CHO}{|}}$ (benzene ring) $\xrightarrow{Conc.\ NaOH}$

(xi) $H_2N-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ $\xrightarrow{\Delta}$

(xii) [calcium dipropionate salt] $\xrightarrow{\Delta}$

(xiii) Cl—H₂C—C₆H₄—Cl $\xrightarrow{Moist\ Ag_2O}$

(xiv) (CH₃)₂C(OH)CH₂CH₃ + ZnCl₂ + Conc. HCl $\longrightarrow$

P.T.O.

(xv)    $\begin{array}{c} H_3C \\ \phantom{} \\ H_3C \end{array} C=O$   +   $Ph_3P=C \begin{array}{c} CH_3 \\ \phantom{} \\ CH_2CH_3 \end{array}$   $\xrightarrow{\Delta}$

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : 4510      G

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.

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

$E^{\circ}_{Cu^{2+}|Cu} = 0.337 \, V$; $E^{\circ}_{Cr^{3+}|Cr} = -0.774 \, V$

$E^{\circ}_{Fe^{3+},Fe^{2+}|Pt} = 0.771 \, V$; $E^{\circ}_{MnO_4^-|Mn^{2+}|H^+} = 1.51 \, V$;

$E^{\circ}_{Cd|[Cd(NH_3)_4]^{2+}} = -0.61V$; $E^{\circ}_{Cd^{2+}|Cd} = -0.40 \, V$.

## Section A

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

   (i) In water system, fusion curve of ice is inclined towards pressure axis. Explain. (3)

   (ii) Ice and common salt mixtures can be used for producing temperatures as low as $-21.1°C$. Explain. (3)

   (iii) Is it possible to separate an azeotropic mixture into two pure components by isobaric fractional distillation? Explain. (3)

   (iv) What are reversible cells? Explain with an example. (3)

   (v) The effect of temperature and pressure on adsorption process is in accordance with Le Chatelier's principle. Explain. (3)

(vi) Polarities of cathode and anode in a galvanic cell are opposite to those in an electrolytic cell. Explain giving reasons. (3)

(vii) The e.m.f. of the hydrogen electrode is linearly dependent only on the pH of the solution. Explain. (3)

2. (i) The absence of a few components in some phases does not alter the phase rule relation, $F = C - P + 2$. Derive the above conclusion by taking the following system of *three* components distributed over *four* phases : (4)

| B+C | A+C+B | A+B+C | A+B+C |
|---|---|---|---|
| Phase I | Phase II | Phase III | Phase IV |

(ii) The steam distillation of a liquid X with molar mass 120 g mol$^{-1}$ is observed to occur at a temperature of 89.0°C when the total pressure is 0.911 bar. Assuming complete immiscibility of this liquid with water, calculate the mass of X in 200 g of distillate. The vapour pressure of water at 89.0°C is 0.6747 bar. (4)

(iii) Derive the Langmuir adsorption isotherm for a gas on a solid and discuss the limiting cases. (4)

3. (i) Starting with the Duhem-Margules equation, derive a relation to show that the vapour phase is richer in the more volatile component for a binary system A-B. (4)

   (ii) With the help of a suitable diagram, discuss the fractional distillation process of a two-component system which exhibits negative deviation from ideal behaviour. (4)

   (iii) On heating a mixture of m-toluidine and glycerol, turbidity appears at $t_1$ and on further heating turbidity is lost at $t_2$. Plot the phase diagram on the basis of the data and report the upper and lower consolute temperatures. Label the various regions with the number of phases and degrees of freedom. (4)

| Mass % of m- toluidine | 18 | 20 | 40 | 60 | 80 | 85 |
|---|---|---|---|---|---|---|
| $t_1(^\circ C)$ | 48 | 18 | 8 | 10 | 19 | 25 |
| $t_2(^\circ C)$ | 53 | 90 | 120 | 118 | 83 | 53 |

4. (i) State and derive Lever rule. (4)

   (ii) Solute (X) shows normal molecular mass in water and is associated in benzene. Find the order of association from the following data

on the distribution of (X) between water and benzene : (4)

| Concentration in $H_2O$, g $L^{-1}$ | Concentration in Benzene, g $L^{-1}$ |
|---|---|
| 0.020 | 0.1025 |
| 0.042 | 0.452 |
| 0.064 | 1.049 |
| 0.122 | 3.811 |

(iii) Derive the integrated form of Clausius-Clapeyron equation for liquid-vapour equilibrium. (4)

5. (i) Explain, giving reasons : (4)

(a) A eutectic mixture has a definite composition and a sharp melting point yet it is not a compound.

(b) Succinic acid alters the C.S.T of phenol-water system when added as impurity at constant pressure.

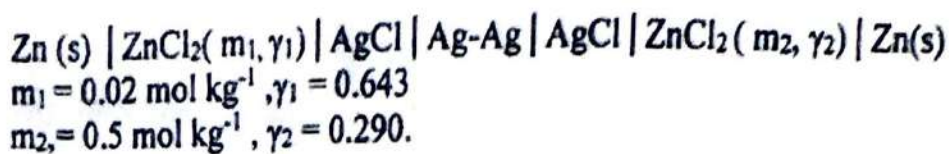(ii) Au and Sb melt at 1060°C and 630°C respectively and form a compound $AuSb_2$, which melts congruently at 850°C. Two eutectic points are observed – one at 10 mol % Au at temperature 530°C and the other at 50 mol % Au at 700°C. Sketch the simplest phase diagram consistent with the information and label all the phase regions. Draw a cooling curve for a melt containing 60 mol % of Sb. (6)

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(iii) Explain the statement "physisorption does not occur at temperatures that are much above critical temperature of adsorbate".                (2)

## Section B

6.    (i) Find the cell reaction and calculate the potential of the following cell at 298 K.                (4)

Zn (s) | ZnCl$_2$( m$_1$, $\gamma_1$) | AgCl | Ag-Ag | AgCl | ZnCl$_2$ ( m$_2$, $\gamma_2$) | Zn(s)
m$_1$ = 0.02 mol kg$^{-1}$ ,$\gamma_1$ = 0.643
m$_2$,= 0.5 mol kg$^{-1}$ , $\gamma_2$ = 0.290.

(ii) Derive an expression for calculating liquid junction potential for a cell in which electrodes are reversible with respect to cation.        (4)

(iii) Predict whether following data of adsorption of acetic acid over 1 g of charcoal at 25°C follows Freundlich adsorption isotherms. Also determine its constants k and n.                (4)

| [acid]/mol L$^{-1}$ | 0.05 | 0.1 | 0.5 | 1.0 |
|---|---|---|---|---|
| Mass adsorbed/g | 0.04 | 0.06 | 0.12 | 0.16 |

7.    (i) Using Gibbs-Helmholtz equation derive the expressions for $\Delta G$ and $\Delta H$.                (4)

(ii) The emf of the cell (4)

$$Ag \mid AgCl(s) \mid KCl\ (aq) \mid Hg_2Cl_2(s) \mid Hg$$
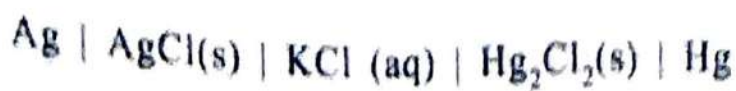
is 0.0421V at 298 K and the temperature coefficient is $3.4\times10^{-4}V\ K^{-1}$. What is the reaction taking place in the cell and what are the free energy, enthalpy and entropy changes at 298 K.

(iii) Describe a glass electrode. What are its limitations? Explain, how the pH of a solution is determined using a glass electrode. (4)

8. (i) The potential of Hamed cell (4)

$$Pt\ (s) \mid H_2(g) \mid HCl\ (aq,m) \mid AgCl\ (s) \mid Ag$$
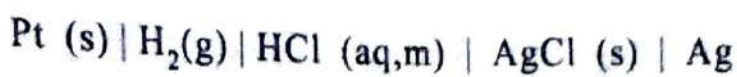
at 25°C has the following values. Determine the standard electrode potential of silver-silver chloride electrode.

| $m/10^{-3}$ | 3.215 | 5.619 | 9.138 |
|---|---|---|---|
| $E_{cell}/V$ | 0.520 | 0.49257 | 0.46860 |

(ii) Discuss the criteria of spontaneity of a cell reaction in terms of cell potential. In which direction will the following reactions be spontaneous when all concentrations are unity? Give reason. (4)

(a) $2Cr + 3Cu^{2+} \rightleftharpoons 2Cr^{3+} + 3Cu$

(b) $Mn^{2+} + 4H_2O + 5Fe^{3+} \rightleftharpoons MnO_4^- + 8H^+ + 5Fe^{2+}$
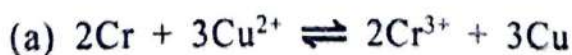
(iii) Derive the following relation between the pressure required to produce a fixed amount of adsorption and the enthalpy of adsorption. Explain how it can be used to determine the enthalpy of adsorption of a gas on solid.

$$\ln\left(\frac{p}{p^0}\right) = \frac{\Delta_{ads}H}{R}\frac{1}{T} + constant \tag{4}$$

9. (i) Determine the standard equilibrium constant for the following reaction at 298 K.

$$Cd^{2+} + 4\ NH_3 \leftrightarrow [Cd(NH_3)]_4^{2+} \tag{4}$$

(ii) What is a reference electrode? Give one example; write its cell representation and Nernst equation. (4)

(iii) Justify the following statements : (4)

(a) If the standard potential of $E^0_{M^{n+}|M}$ is positive, then $M^{n+}$ ions can be reduced to M by hydrogen gas under standard conditions.

(b) Instead of pieces of charcoal, activated charcoal is used in adsorption studies.

(1000)

[This question paper contains 4 printed pages.]

Sr. No. of Question Paper : 4324      **G**

Unique Paper Code     : 32171501

Name of the Paper     : Organic Chemistry IV : Biomolecules

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

Semester               : V

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 **6** questions.

3. **All** Questions carry equal marks.

1. (a) (i) Give the sequence of reactions to establish the pyranose ring size in glucose? (3)

     (ii) Draw Fisher projection and Haworth structure of $\beta$-D-Fructofuranose. (3)

(b) A pentapeptide, X with empirical composition, Phe-2, Lys, Trp, Tyr was recovered unchanged on treatment with Trypsin. DNFB treatment of X

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followed by hydrolysis gave DNP-Tyr. Partial acid hydrolysis of X gave two tripeptides with the following amino acid composition :

1. Phe,Tyr,Trp

2. Phe, Trp,Lys

Elucidate the sequence of amino acids in X. Give the products of treatment of X with Chymotrypsin.

(6.5)

2.  (a) Draw the complimentary DNA sequence of the given fragment specifying the direction 5'—ATGC—3'. (4.5)

(b) Draw the structure of glyceryl trilinoleate and calculate its iodine value. (4)

(c) Fructose contains a ketonic group, yet it reduces Tollens' reagent and Fehling's solution. Why? Give the mechanism and name of reaction involved. (4)

3.  (a) (i) How is pyruvate converted to ethanol under anaerobic conditions? Name the enzyme and give the reaction involved. (3.5)

(ii) ATP is called the universal currency of cellular energy. Explain giving its hydrolytic pathway. (3)

(b) Give the complete name and structure of

(i) dAMP

(ii) UDP (4)

(c) What are cofactors? Give an example. (2)

4. (a) Give the structure of the disaccharide sucrose. What is its IUPAC name? Account for the observation that it does not reduce Fehling's solution and it does not mutarotate. (3)

(b) Give the mechanism of osazone formation for D-glucose. D-Glucose and D-Fructose give the same osazone. Explain. (3.5)

(c) How would you synthesize the tripeptide, Ala-Gly-Ala using solid phase peptide synthesis. (6)

5. (a) Explain the mechanism of action of chymotrypsin. (6)

(b) What are drying and non-drying oils? Give one example of each type. (4)

(c) What is denaturation of protein? How it is caused? (2.5)

6. (a) An α- D – methylglycoside, X, with molecular formula $C_7H_{14}O_6$, consumes 2 moles of $HIO_4$ and gives one mole of HCHO. Arrive at possible structure/s of X. (4)

P.T.O.

(b) Define genetic code. Give at least three characteristics of genetic code. (4.5)

(c) Differentiate between competitive and non-competitive enzyme inhibition and give examples of each kind. (4)

7. (a) Discuss various steps involved in the glycolysis cycle, giving the names of enzymes and structures of intermediates. (6)

(b) List any two reactions that were not explained by the open chain structure of glucose. How does the cyclic hemiacetal structure of glucose explain them. (4)

(c) Define ω – fatty acids giving suitable example. (2.5)

8. (a) How will you convert :

    (i) D-Glucose to D- Arabinose.

    (ii) D-Glucose to D-Fructose. (4.5)

(b) List four important characteristic of Watson and Crick model of DNA. (4)

(c) Discuss the 2° structure of proteins. (4)

**(1000)**

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

Sr. No. of Question Paper : 4378     G

Unique Paper Code : 32171502

Name of the Paper : Physical Chemistry V: Quantum Chemistry & Spectroscopy

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

Semester : V

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, **three** questions each from sections **A** and **B**.

3. Attempt all part of a question together.

4. **All** questions carry equal marks.

5. Use of a non-programmable scientific calculator is allowed.

P.T.O.

## Physical constants

| | |
|---|---|
| Atomic mass unit | $= 1.66 \times 10^{-27}$ kg |
| Planck's constant | $= 6.626 \times 10^{-34}$ J s |
| Velocity of Light | $= 3 \times 10^{8}$ m s$^{-1}$ |
| Boltzmann constant | $= 1.381 \times 10^{-23}$ J K$^{-1}$ |
| Mass of Electron | $= 9.1 \times 10^{-31}$ kg |
| Avogadro's number | $= 6.023 \times 10^{23}$ mol$^{-1}$ |
| Nuclear magneton | $= 5.05 \times 10^{-27}$ J T$^{-1}$ |
| Bohr magneton | $= 9.274 \times 10^{-24}$ J T$^{-1}$ |

## Section A

### (Quantum Chemistry)

1. (a) The uncertainty in a quantity, represented by operator A is given as under,

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2$$

For a particle in the ground state of a one-dimensional box having length, L, represented by

$$\psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} \sin\left(\frac{\pi x}{L}\right), \quad \text{determine } \sigma_x \cdot \sigma_p$$

where x and p represent position and momentum, respectively.

Use standard integral $\int x \sin\left(\dfrac{\pi x}{L}\right) = \dfrac{L^2}{4}$ and

$$\int x^2 \sin^2\left(\frac{\pi x}{L}\right) = \left(\frac{L}{2\pi}\right)^3 \left(\frac{4\pi^3}{3} - 2\pi\right).$$

(b) Prove that the functions having different real eigen values for linear momentum operator are orthogonal.

(c) Starting from $\left[\dfrac{d}{dx}, x\right] = 1$, use the commutator identities to find

    (i) $[\hat{x}, \widehat{p_x^2}]$

    (ii) $[\hat{x}, \hat{H}]$, $\hat{H}$ is Hamiltonian for a one-particle, three-dimensional system.     (4.5,4,4)

2. (a) Demonstrate that the Eigen functions for the particle in a one-dimensional box are orthonormal.

$$\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

(b) Write Hamiltonian operators for a particle moving under constant potential 'V' in a (i) one-dimensional box and (ii) three-dimensional box.

(c) As a crude treatment for the $\pi$ electrons of a conjugated polyene, the $\pi$ electrons of the conjugated chain are considered as moving in a one-dimensional box across the end to end conjugated chain. Considering 1,3-butadiene as a one-dimensional box of box length, 7.0 Å, calculate the wavelength of light absorbed when a $\pi$ electron is excited from the highest-occupied to the lowest-vacant level of the molecular electronic ground state.       (4.5,4,4)

3.   (a) Construct the Hamiltonian operator for Simple Harmonic oscillator and write the Schrodinger equation. What is the zero-point energy of this type of system?

(b) A molecule X has 10 pi electrons and it is assumed to have cubical shape with edge length 10 pm. Give the quantum numbers corresponding to the highest occupied energy levels. Based on the free electron model, calculate the longest wavelength required for transition.

(c) Normalize the following functions :

    (i) $f(r) = r \exp(-ar)$    $0 \leq r \leq \infty$

    (ii) $f(\varphi) = N \exp(im\phi)$    $0 \leq \varphi \leq 2\pi$

                                          (4.5,4,4)

4.    (a) Using linear momentum operator $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$, derive angular momentum operators, $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$. Using $\hat{L}_z = -i\dfrac{h}{2\pi}\left(\dfrac{d}{d\phi}\right)$ construct the Schrodinger equation dependent on variable $\varphi$ only. Write a possible solution as an eigen function and determine eigen values.

(b) Using normalized ground state wave function for hydrogen atom

$$\psi(r) = 2\left(\frac{1}{a}\right)^{3/2} \exp\left(\frac{-r}{a}\right)$$

Determine

    (i) $\langle E \rangle$

    (ii) The radius of maximum radial density distribution of electron

                                                      P.T.O.

(c) Why do we need to employ approximate methods to determine solution for multielectron atoms? Explain Variation principle as an approximate method' to determine approximate wave function.

(4.5,4,4)

## Section B

### (Molecular Spectroscopy)

5. (a) A molecule $AB_2$ has the following infra-red and Raman spectra :

| Wave number ($cm^{-1}$) | Infrared | Raman |
|---|---|---|
| 589 | Active (PQR) | Inactive |
| 1285 | Active (PR) | Active (polarized) |
| 2224 | Active (PR) | Active (depolarized) |

Giving proper explanation and arrive at the geometry of the molecule. Assign the wavenumbers to specific vibrations.

(b) The intensities of Stokes and anti-Stokes lines are similar in rotational Raman spectra. However, in the vibrational Raman spectra, the Stokes lines are more intense than the anti-Stokes lines. Explain.

(c) Discuss how a simple harmonic oscillator system differs from a homonuclear diatomic molecule undergoing anharmonic oscillations in terms of energy relation and energy vs displacement curve from mean position. (4.5,4,4)

6. (a) Given that the spin quantum numbers of $^{12}C_6$, $^1H_1$ and $^2D_1$ are zero, half and one, respectively, how many different energy states do these nuclei have in a magnetic field? Which of these atoms will show peak in the NMR spectra?

(b) Draw and discuss, the low and high-resolution NMR spectrum of $CH_3CHO$ showing the peak corresponding to the reference standard TMS.

(c) The pure microwave spectrum for $^1H^{35}Cl$ is observed as a series of lines at 20.7, 41.5, 62.0, 83.0, 103.8 cm$^{-1}$. Evaluate the rotational constant and the internuclear distance for this molecule. (4.5,4,4)

7. (a) What do you understand by the terms, 'singlet' and 'triplet'? On the basis of these terms explain why fluorescence is a rapid phenomenon as compared to phosphorescence.

(b) Explain Larmor precession of a spinning nucleus and derive expression for precessional frequency.

(c) The spacing between the successive lines of Raman rotational spectrum of $O_2$ molecule is 8B while for $H_2$ molecule it is 4B (where B is the rotational constant). Explain. (4.5,4,4)

8. (a) What is Fermi Resonance and hot bands in IR spectroscopy.

(b) Write short notes on the following:

   (i) Dissociation and Predissociation

   (ii) Franck Condon principle (4.5,4+4)

[This question paper contains 8 printed pages.]

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

**Sr. No. of Question Paper : 1545**          G

Unique Paper Code          : 2172011101

Name of the Paper          : DSC: Atomic Structure & Chemical Bonding (Inorganic Chemistry I)

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

Semester          : I

Duration : 3 Hours          Maximum Marks : 90

## Instructions for Candidates

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

2. Attempt **six** questions.

3. **Question no. 1** is compulsory.

4. **All** questions carry equal marks.

P.T.O.

1. Attempt **any five** of the following

(i) What is meant by Dipole moment? Can its magnitude give an idea about the structure of molecules? Explain.

(ii) Why NaCl is soluble in water but AgCl is not?

(iii) The first electron ionization enthalpy of boron (B) is smaller than that of carbon (C) whereas the second electron ionization enthalpy of carbon is smaller than boron.

(iv) Orbitals of 1p, 2d, 4g not possible.

(v) The electron gain enthalpy of chlorine (Cl) is greater than fluorine (F).

(vi) Calculate the effective nuclear charge of 4s and 3d electron in Scandium using Slater's rule.

$(5 \times 3)$

2. (i) Write the time independent Schrödinger wave equation for hydrogen atom and explain the terms used in it.

(ii) Why half filled and fully filled configurations are more stable than the other configurations.

(iii) Draw Born Haber Cycle and calculate the enthalpy of formation ($\Delta H_f$) for $MgF_2$ using following data,

Sublimation Enthalpy of Mg = 146. 4 kJ/mol

Ionization Enthalpy of Mg to $Mg^{2+}$ = 2184 kJ/mol

Dissociation Energy of $F_2$ = 158.9 kJ/mol

Electron gain enthalpy of F(g) = -334.7 kJ/mol

P.T.O.

Lattice Energy of $MgF_2$ = -2922.5 kJ/mol

(iv) Calculate the limiting radius ratio ($r^+/r^-$) of an ionic lattice having the octahedral geometry with co-ordination number 6 around cation.

(2.5×2,5,5)

3. (i) What is normalized and orthogonal wave function? Write the mathematical expression for normalization and orthogonality of wave function.

(ii) The bond angle in $CH_2F_2$, HCH = 112.3° and FCF = 108.3°. Calculate the s character used by carbon atom in the orbital directed to the hydrogen and fluorine. Discuss the result in terms of Bent rule.

(iii) Draw the shape of the following molecules using VSEPR theory.

$ClF_3$, $BrF_2^+$ +, $PCl_3$, $SnCl_2$, $OF_2$                (5,5,5)

4. (i) Calculate ionic radii for $Na^+$ & $K^+$ ions if the internuclear distance in NaF is 231 pm.

(ii) The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the $n = 1$ orbit. Calculate the wavelength of the lowest-energy line in the Lyman series. In what region of the electromagnetic spectrum does it occur?

(iii) Draw the molecular orbital diagram of $N_2$ and $O_2$ molecules and explain their magnetic behavior.

(5,5,5)

5. (i) Based on their positions in the periodic table, arrange these ions in order of increasing radius: $Cl^-$, $K^+$, $S^{2-}$, and $Se^{2-}$

P.T.O.

(ii) The bond distance between H and F in HF molecule is 91.7 pm and the experimentally observed dipole moment of this molecule is $6.6 \times 10^{-30}$ Cm. Find out the percent ionic character.

(iii) Write the Born Lande equation and the Kapustinskii equation for lattice energy and define the terms involved. What is the advantage of Kapustinskii over Born Lande equation? (5,5,5)

6. (i) Calculate the electronegativity of F from the following data, electronegativity of hydrogen is 2.1, $E_{F-F}$ bond dissociation energies = 36.6 kcal/mol, $E_{H-H}$ = 104.2 kcal/mol, $E_{H-F}$ = 136.6 kcal/mol.

(ii) Draw the radial distribution curve of 1s, 2s, 2p, 3p, and 3d.

(iii) Draw the MO diagram of CO with sp mixing. On the basis of it, explain it is an electron pair donor.

(5,5,5)

7. (i) What is resonance? Draw the resonating structure of $NO_2$, CO and $O_3$.

(ii) Write the conditions for a wave function $\psi$ acceptable to the Schrodinger wave equation. What is the physical significance of $\psi$ and $\psi^2$.

(iii) How will you convert the Cartesian co-ordinates (x, y, z) into polar co-ordinates (r, θ, φ)

(5,5,5)

8. (i) Write short notes (any two)

(a) Heisenberg Uncertainty Principle

P.T.O.

(b) Equivalent and Non-equivalent hybrid orbitals.

(c) Different scales of electronegativity.

(ii) Which of the following combinations are allowed in LCAO (considering Z axis as molecular axis) and sketch the shapes of molecular orbitals formed by their addition and subtraction

(a) s and $p_z$

(b) $p_x$ and $p_x$

(iii) List the limitations of:

(a) Bohr's Theory of atomic structure.

(b) Radius ratio rule.          (5,5,5)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 1583      G

Unique Paper Code          : 2172011102

Name of the Paper         : DSC – Basic Concepts and Aliphatic Hydrocarbons (Organic Chemistry I)

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

Semester                   : I
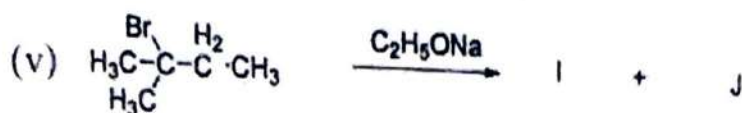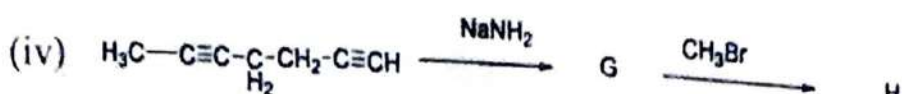
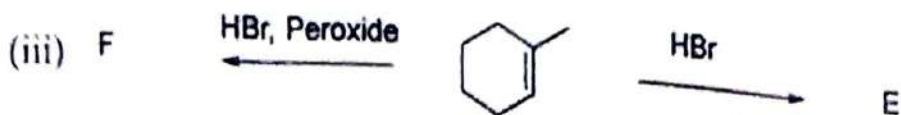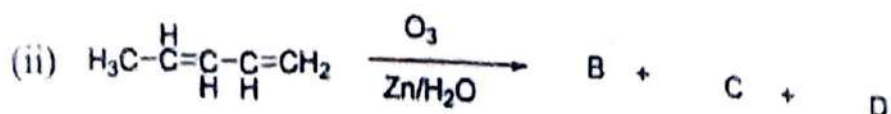Duration : 3 Hours             Maximum Marks : 90

## Instructions for Candidates

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

2. Attempt any **six** questions.

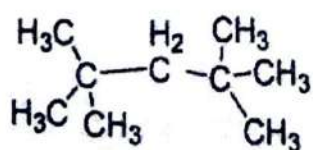3. Each question carries **15** marks.

1. Complete the following :

(i)  $\longrightarrow$     A

P.T.O.

(ii) $H_3C-\overset{H}{\underset{H}{C}}=C-\underset{H}{C}=CH_2$ $\xrightarrow[Zn/H_2O]{O_3}$ B + C + D

(iii) F $\xleftarrow{\text{HBr, Peroxide}}$  $\xrightarrow{\text{HBr}}$ E

(iv) $H_3C-C\equiv C-\underset{H_2}{C}-CH_2-C\equiv CH$ $\xrightarrow{NaNH_2}$ G $\xrightarrow{CH_3Br}$ H

(v) $H_3C-\overset{Br}{\underset{H_3C}{C}}-\overset{H_2}{C}\cdot CH_3$ $\xrightarrow{C_2H_5ONa}$ I + J
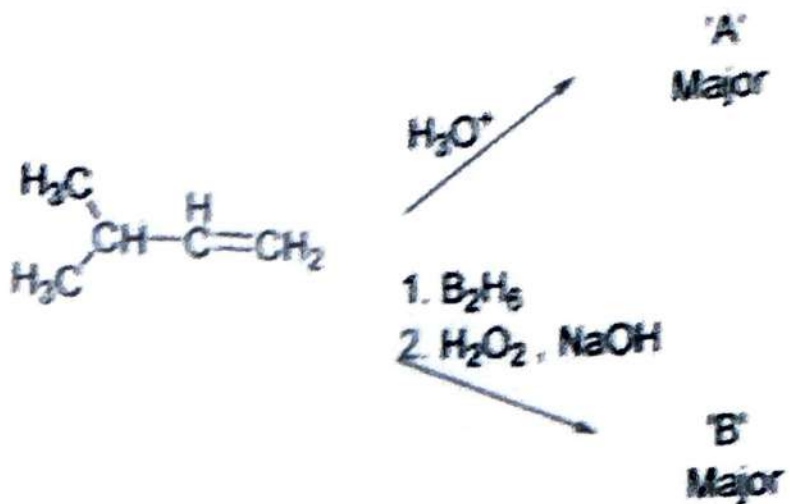
(1.5 marks for each product)

2. (i) Predict the proportion of isomeric products obtained at room temperature from chlorination of the given molecule. The order of reactivity of hydrogen for chlorination is 3° (5.0): 2° (3.8): 1°(1.0)

$$H_3C\underset{H_3C}{\overset{}{\diagdown}}\overset{H_3C}{\underset{CH_3}{C}}-\overset{H_2}{\underset{}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

(ii) Define specific rotation. A solution of compound 'A' (7.14 g in 100 mL) in chloroform was taken in a polarimeter tube (5 cm) and its optical rotation at 25°C is −1.3°. Calculate the specific rotation of compound 'A'.

(iii) Explain the formation of different products, (A) and (B) in the given reactions given below :

$$\underset{H_3C}{\overset{H_3C}{\diagdown}}CH-\overset{H}{\underset{}{C}}=CH_2$$

$\xrightarrow{H_3O^+}$ 'A' Major

$\xrightarrow[\text{2. } H_2O_2, \text{ NaOH}]{\text{1. } B_2H_6}$ 'B' Major

(5,5,5)

3. (i) 1,3-Butadiene on treating with HBr at low temperature gives 3-bromobut-1-ene (major product), whereas at high temperature, it gives 1-bromobut-2-ene (major product). Explain with mechanism.

(ii) An alkyl halide 'A' ($C_4H_9Br$) reacts with ale. KOH and gives an alkene, B. Compound B reacts with bromine to give compound 'C' Compound 'C' on treatment with excess of sodamide forms compound 'D'. Further, compound 'D' on

P.T.O.

reaction with ammoniacal $AgNO_3$ solution, gives a precipitate (E). Write the structures of A, B, C, D and E.

(iii) Write the structure of 'X' and give the mechanism for its formation.

$$Cl_3C-\underset{H}{C}=CH_2 \quad + \quad Br_2 \quad \xrightarrow{H_2O} \quad X$$
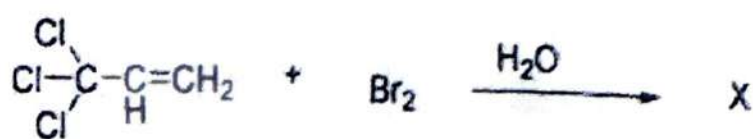
(5,5,5)

4. (i) Draw the Fischer projections formula of threo- and eythro-2,3-butanediol and convert them into corresponding Sawhorse projection formula.

(ii) Draw the possible chair conformations of 1-methylcyclohexane and compare their stability.

(iii) Arrange the following compounds in increasing order of acidity and explain the order.

$CH_3COOH$      $HCOOH$      $C_6H_5CH_2COOH$
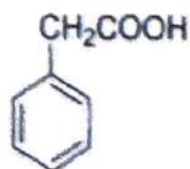
(5,5,5)

5.  (i)  Draw the Fischer projection of all the possible stereoisomers of 2,3-dichlorobutan-1,4- dioic acid. Comment on optical activity of each isomer.

(ii)  How would you resolve a racemic mixture of a primary amine ($\pm RNH_2$) using the formation of diastereomeric salt?

(iii)  Arrange the following carbocations in increasing order of stability and explain the order.
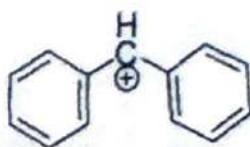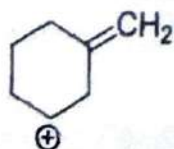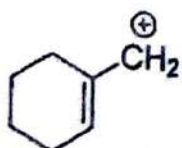


(5,5,5)

6.  (i)  Considering the C2-C3 bond rotation in n-butane, draw the potential energy profile for its various conformations.

P.T.O.

(ii) (a) Why maleic acid has lower melting point than fumaric acid?

(b) Arrange the following compounds in increasing order of their boiling points and explain the order.

2-methylbutane, 2,2-dimethylpropane and pentane.

(iii) What is allylic halogenation? Give the reason for the products obtained when propene reacts with a) $NBS/CCl_4$ and b) $Br_2$ at room temperature.                (5,5,5)
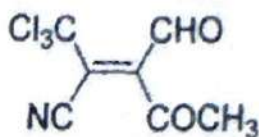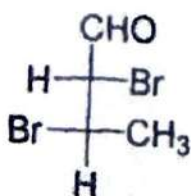
7.    (i) Find the number of sigma and pi bonds in the given molecule.
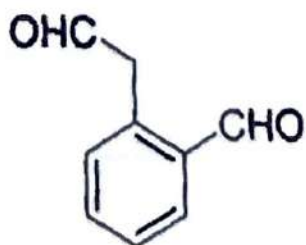
(ii) Which of the following compounds is more stable and why?



(iii) How Corey-House synthesis overcomes the limitation of Wurtz reaction?

(iv) Assign the priority order and find R/S or E/Z configuration for the given molecules:



(3,3,3,6)

8. (i) Write the reaction for hydration of 2-pentyne.

(ii) Give a test to differentiate between 1-butyne and 1-butene.

(iii) Which of the following will exhibit geometrical isomers? Explain by drawing structures.

2-Butene; 2-methyl-2-butene and 2-pentene

P.T.O.

(iv) Differentiate between the following with suitable examples **(any two)** :

(a) Inductive effect and electrometric effect

(b) Relative and absolute configuration

(c) Electrophile and nucleophile                (3,3,3,6)

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

Sr. No. of Question Paper : 1621     G

Unique Paper Code     : 2172011103

Name of the Paper     : DSC: Gaseous and Liquid State (Physical Chemistry I)

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

Semester     : I

Duration : 2 Hours     Maximum Marks : 60

## Instructions for Candidates

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

2. Use of a scientific calculator and log table is allowed.

3. Attempt **four** questions out of **six**, question number **one** is compulsory.

   ($R = 8.314 \, KJ^{-1} \, mol^{-1}$    $k = 1.38 \times 10^{-23} \, KJ^{-1}$    $N_A = 6.023 \times 10^{23} \, mol^{-1}$)

1. Attempt any **Five** of the following :

   (a) An ideal gas is not expected to show any cooling on free expansion. Explain.

   (b) Define the mean free path. Predict mean free path at high vacuum.

   (c) Explain why the viscosity of ethyl alcohol is greater than that of ether.

P.T.O.

(d) Addition of detergent decreases the surface tension of water while NaCl addition increases the surface tension of water. Comment.

(e) Show that van der Waals constant $b$ for a real gas is four times its molecular volume.

(f) Write the formula of average speed, most probable speed, root mean square speed and arrange them in increasing order.

(3×5)

2. (a) Derive an expression for the kinetic gas equation, in terms of the mass of a molecule (m), the total number of molecules (N), and the velocity of the molecule (c).                                                  (5)

(b) Derive the reduced equation of state for a real gas using the expressions of the critical constants assuming that gas follows van der Waals equation of state. Is this equation applicable to all gases?

(5)

(c) For a gas containing $10^{23}$ gas particles each of mass $10^{-25}$ kg in a container of volume $10^{-3}$ m$^3$. Calculate

(i) The pressure exerted by the gas.

(ii) The total kinetic energy of molecules.

(iii) Temperature of the gas.

Given : Root mean square speed is $10^5$ cm s$^{-1}$.

(5)

3. (a) For oxygen gas at 25 °C and 1 atm pressure calculate.

    (i) Mean free path,

    (ii) Number of collisions per second per molecule

    The collision diameter of oxygen molecule is 361 picometre.         (5)

    (b) Discuss the effect of height, temperature and molecular mass of the gas on barometric distribution of gases.         (5)

    (c) (i) Write the mathematical expression for Maxwell's distribution of molecular speeds for a gas explaining briefly the terms involved.

        (ii) Derive the expression for the average speed of a gas.         (5)

4. (a) The critical constants for water are 647 K, 22.09 MPa and 0.0566 dm$^3$ mol$^{-1}$. Calculate the values of van der Waals constants a, b and R and also explain the abnormal value of R.         (5)

    (b) Write the van der Waals equation in the virial form and evaluate the second virial coefficient.         (5)

    (c) Explain the Andrews isotherms for a real gas. Derive the relations between van der Waals constants and critical constants.         (5)

P.T.O.

5.    (a) Define the surface tension of a liquid, give its unit and describe in detail its determination using a stalagmometer.      (5)

     (b) When a capillary is dipped in a liquid, some liquids rise in the capillary whereas some others fall. Explain the reason behind this phenomenon. What are these liquids called? Give one example of each. Give one example from your daily life where this phenomenon is observed.      (5)

     (c) Benzene has a density of 0.879 g cm$^{-3}$ and has a surface tension of 0.02888 N m$^{-1}$. What will be the difference of its heights in two capillaries of radii 0.10 mm and 0.15 mm, respectively?      (5)

6.    (a) Calculate the pressure exerted by one mole of oxygen gas at 298 K, contained in a container of volume 5 litres, if the gas is a) ideal, b) van der Waals gas. Given $a$ = 5.5 L$^2$ atm mol$^{-1}$, $b$ = 63.8 cm$^3$ mol$^{-1}$, R = 0.082 L atm K$^{-1}$ mol$^{-1}$.      (5)

     (b) How is vapour pressure of a liquid related to its boiling point? Discuss the effect of external pressure and non-volatile impurities on the boiling point of a liquid.      (5)

     (c) Explain how the viscosity of a liquid varies with temperature ? Support your answer with the mathematical relation between viscosity and temperature. Does viscosity of a gas also show the same variation with temperature?      (5)

**(1000)**

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

Sr. No. of Question Paper : 1526      G

Unique Paper Code      : 2172012301

Name of the Paper      : DSC: Chemistry of d- and f- Block Elements & Quantitative, Inorganic Analysis

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

Semester      : III

Duration : 2 Hours          Maximum Marks : 60

## Instructions for Candidates

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

2. Attempt *four* questions in all.

3. All Questions carry equal marks.

1. Explain the following giving reasons:

    (a) Transition elements generally show variable oxidation states.

P.T.O.

(b) $CrO_3$ is strongly oxidising while $WO_3$ is stable.

(c) Titanium(III) ions are attracted by the magnetic field, while titanium(IV) ions are repelled.

(d) Clay minerals cleave easily into thin sheets.

(e) Lanthanides show sharp bands in the absorption spectra while transition elements show broad bands. (5x3)

2. (a) Give reason:

(i) Mn(II) ion shows the maximum magnetic character amongst the bivalent metal ions of the 3d series.

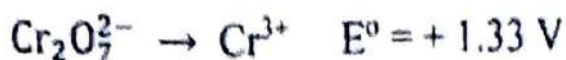(ii) Cu(II) salts are blue while Zn(II) salts are colourless.

(b) Write the electronic configuration and give the number of unpaired electron(s) present in 4f orbitals of the following:
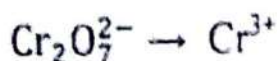
(i) Gadolinium (Atomic number 64)

(ii) Terbium (Atomic number 65)

(c) Actinides have a greater tendency to form complexes than lanthanides. Explain. (3x5)

3. (a) Explain the catalytic properties of transition elements with the help of suitable examples.

   (b) Construct the Latimer diagram for Cr in acidic medium:

   $$Cr_2O_7^{2-} \rightarrow Cr^{3+} \quad E^o = +1.33 \text{ V}$$
   $$Cr^{3+} \rightarrow Cr^{2+} \quad E^o = -0.41 \text{ V}$$
   $$Cr^{2+} \rightarrow Cr \quad E^o = -0.91 \text{ V}$$

   (i) Write half cell reaction for the conversion of:

   $$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

   (ii) Is there any tendency of $Cr^{2+}$ to reduce to Cr? Give reason.

   (iii) Calculate skip step emf for $Cr^{3+} \rightarrow Cr$ change.

   (c) Define Digestion. What is the importance of digestion in gravimetric analysis? (3x5)

4. (a) Explain the separation of lanthanides by ion exchange method.

   (b) What are silicates? Briefly describe various types of silicates with suitable example.

   P.T.O.

(c) What are the conditions of good wash liquid in gravimetric analysis? How will it be ensured that the washing of the precipitate is complete by means of qualitative method?

(3x5)

5. (a) What is Lanthanide contraction? What are the major consequences of lanthanide contraction?

(b) Write a short note on Silicones.

(c) Compare the magnetic properties of transition elements and lanthanides.

(3x5)

6. (a) Draw the structures of the following:

(i) Borax

(ii) cyclic-$[NPCl_2]_3$

(b) What is supersaturation? How it can be kept in low value?

(c) Choose the correct option and give reason for the same.

Greater number of oxidation states: Fe or Mn

Good reducing agent: Ce(II) or Sm(II)      (3×5)

(1000)

Sr. No. of Question Paper : 1564      **G**

Unique Paper Code     : 2172012302

Name of the Paper      : DSC: Carbonyls, Carboxylic Acids, Amines, Nitro Compounds, Nitriles, Isonitriles and Diazonium Salts

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

Semester      : III

Duration : 3 Hours      Maximum Marks : 90

## 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. **All** questions carry equal marks.

1. (a) An organic compound $A(C_5H_8O_2)$ forms a dioxime. It gives a positive Tollen's test. On Clemmensen reduction, it forms n-pentane. It also gives a positive iodoform test to form sodium salt of

P.T.O.

dicarboxylic acid which on acidification gives a dicarboxylic acid B ($C_4H_6O_4$).

(i) Predict the structures of A and B.

(ii) Give the reagent used in Clemmensen reduction.

(iii) Give the reaction involved in the Iodoform test of A to form B.

(iv) What is the chief use of Tollen's test?

(b) An optimum pH is required for the reaction of carbonyl compounds with ammonia derivatives. Justify the statement.

(c) Write the synthesis of the following compounds using Ethyl acetoacetate or Diethylmalonate:

(i) Crotonic acid

(ii) 5,5-Diethylbarbituric acid

(d) Why tertiary amines with three different groups attached to nitrogen atom do not show optical activity? Explain by taking a suitable example.

(4,4,4,3)

2. (a) Amine A ($C_5H_{13}N$) on treatment with methyl iodide followed by silver hydroxide forms compound

B ($C_6H_{17}NO$) which is basic in nature. Compound B on heating forms 1-Propene and amine C ($C_3H_9N$). Identify A, B and C. Give the mechanism of formation of both products from B.

(b) Arrange the following in order of decreasing reactivity towards nucleophilic addition reactions, giving reasons :

$CH_3COCH_3$ ; $C_6H_5COCH_3$ ; HCHO ; $CH_3COCH(CH_3)_2$
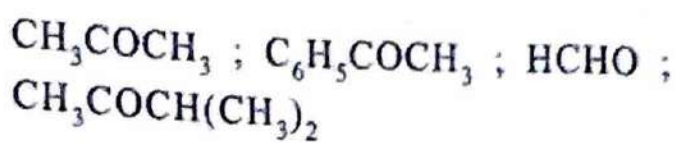
(c) How will you distinguish between the following compounds on the basis of the product they form on heating:

(i) Oxalic acid and Succinic acid

(ii) β-Hydroxy acid and γ-Hydroxy acid

(d) Write the mechanism of Keto-enol tautomerism in an acidic OR alkaline medium.               (4,4,4,3)
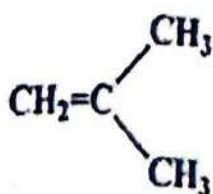
3.   (a) Elaborate :

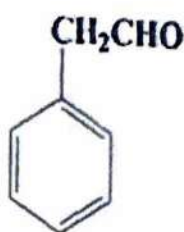(i) p-Hydroxybenzaldehyde does not undergo Cannizzaro reaction.

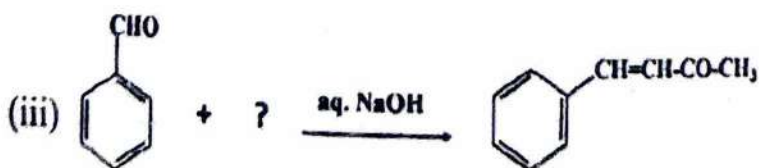(ii) Benzil rearranges to Benzilic acid when treated with a base. Justify on the basis of reaction mechanism.

(b) Outline the synthesis of the given alkene using Wittig reaction :

$$CH_2=C\begin{cases} CH_3 \\ CH_3 \end{cases}$$

(c) Give the product formed and the mechanism involved in the aldol condensation of the given carbonyl compound :

$CH_2CHO$

(d) Complete the following reactions :

(i) $CH_3CH_2CH_2CHO \xrightarrow{\quad LAH \quad}$ ?

(ii) ? + $CH_3-CH-CH_3$ $\underset{OH}{\overset{}{}}$ $\xrightarrow{\quad Al(OiPr)_3 \quad}$ $\overset{HO}{\underset{}{}}$ + $CH_3COCH_3$

(iii) $\overset{CHO}{\bigcirc}$ + ? $\xrightarrow{\quad aq. NaOH \quad}$ $CH=CH-CO-CH_3$
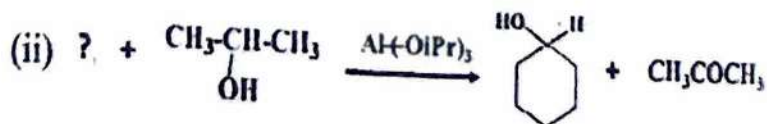
(4,4,4,3)

4. (a) Complete the following sequence of reactions giving structures of A, B, and C. Also give the name of reactions involved in the two sequences:
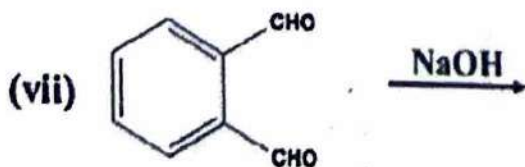
$CH_3CH_2CH_2COOH$ $\xrightarrow{Br_2/Red\ P}$ A

$\left| \begin{array}{l} \text{(i) } SOCl_2 \\ \text{(ii) } NH_3 \end{array} \right.$ → B $\xrightarrow{Br_2/NaOH}$ C
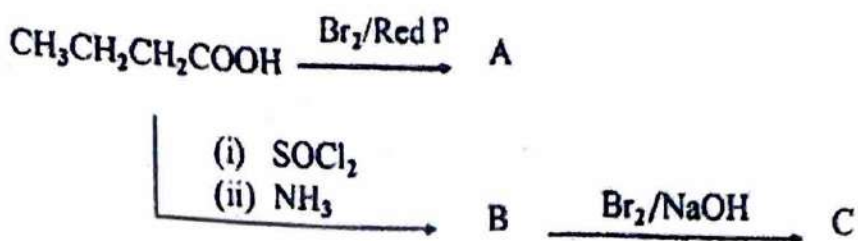
(b) What happens when Acetone is reacted with Ethyl bromoacetate in presence of Zinc. Give the name of reaction along with the mechanism.

(c) All ortho substituted benzoic acids are stronger acids than benzoic acid. Give reason.

(d) Carboxylic acids do not form oxime even though they have $\diagdown C=O$ group in their structure. Give reason.

(4,4,4,3)

5. (a) Arrange the following in increasing order of basicity, give reason to justify your answer :

$C_6H_5NH_2$ ; $m\text{-}OCH_3C_6H_4NH_2$ ; $p\text{-}OCH_3C_6H_4NH_2$

P.T.O.

(b) How will you distinguish between ethylamine, diethylamine and triethylamine using Hinsberg's method? Give the reactions involved.

(c) Outline the preparation of n-propylamine by Gabriel phthalimide synthesis.

(d) Coupling reactions of diazonium salts do not take place in strongly acidic or strongly alkaline conditions. Explain using suitable structures.

(4,4,4,3)

6. (a) Discuss the mechanism of acid-catalysed hydrolysis of nitriles.

(b) Give a reaction to distinguish between nitriles and isonitriles.

(c) Carry out the following conversions : **(Any two)**

    (i) m-Bromotoluene from Toluene

    (ii) o-Chlorophenol from Chlorobenzene

    (iii) Adipic acid from Diethylmalonate

(d) How do primary, secondary and tertiary nitroalkanes react with nitrous acid. Give the reactions involved. (4,4,4,3)

7. (a) Predict the product and give the name of the reaction involved : (Any six)

(i) $CH_3CH=CH-COCH_3 + CH_2(COOEt)_2 \xrightarrow{EtO^-}$

(ii)

$+ ArN_2^+Cl^- \xrightarrow{aq.\ NaOH}$

(iii) $CH_3CH_2CH_2NO_2 \xrightarrow[\text{(ii) } H_2SO_4/boil]{\text{(i) NaOH}}$

(iv) $CH_3CH_2CH_2\overset{+}{N}(CH_3)_2 \xrightarrow{\Delta} A + B$
　　　　　　　　　　$\overset{|}{O^-}$

(v)

$\xrightarrow{CF_3COOOH}$

(vi) $C_6H_5NH_2 + CHCl_3 + 3\ KOH \longrightarrow$

(vii)

$\xrightarrow{NaOH}$
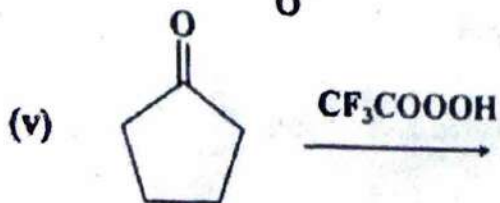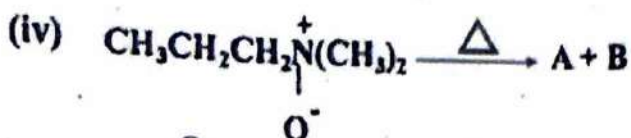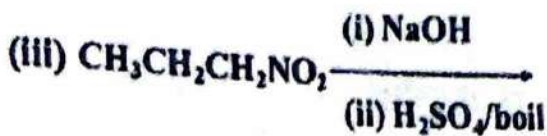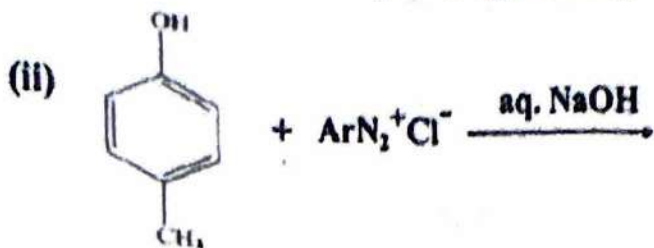
(b) 1,6-diesters undergo cyclization when treated with sodium ethoxide. Write the name of the reaction and its mechanism. (2×6,3)

8. (a) Write short notes (Any three)

  (i) Benzoin condensation

  (ii) Beckmann rearrangement

  (iii) Alkaline ester hydrolysis

  (iv) Thorpe nitrile condensation

 (b) Write the final product formed in reduction of nitrobenzene under the following conditions :

  (i) Sn/HCl

  (ii) Zn/NH$_4$Cl

  (iii) Electrolytic reduction    (4,4,4,3)

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

Sr. No. of Question Paper : 1602        G

Unique Paper Code      : 2172012303

Name of the Paper     : DSC: Chemical Equilibrium, Ionic Equilibrium, Conductance and Solid State

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

Semester             : III

Duration : 3 Hours          Maximum Marks : 90

## Instructions for Candidates

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

2. Attempt any 6 questions in all.

3. Use of scientific calculator is permitted.

4. Graph paper will be provided.

   Values of constant: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ Or 1.987 Calorie $\text{K}^{-1} \text{ mol}^{-1}$ Or 0.082 atm $\text{dm}^3 \text{K}^{-1} \text{mol}^{-1}$; $F = 96500$ $\text{C mol}^{-1}$

P.T.O.

1. (a) Explain :

     (i) pH of neutral water at 110°C is less than 7 but it is not acidic in nature.

     (ii) Addition of barium chloride to sodium sulphate solution precipitate out barium sulphate but not sodium chloride.

(b) Calculate the pH of the following solution:

     (i) 0.030 M Ba (OH)$_2$ solution.

     (ii) pH of 0.002 M acetic acid if it is 2.5% ionized at this dilution.

(c) Define hydrolysis. Discuss hydrolysis of a salt of weak acid and weak base and derive pH of this aqueous salt solution is :

$$pH = \frac{1}{2} \left( pK_w + pK_a - pK_b \right)$$

(d) Write expression for ionization constant for the different stages of dissociation of sulphuric acid. Explain why 2$^{nd}$ ionization constant is less than 1$^{st}$ ionization constant.      (4,4,4,3)

2. (a) Define solubility and solubility product. State the principle of solubility product. How is the solubility of a salt affected by the presence of a common ion?

(b) A litre of solution containing 0.1 mole of acetic acid ($CH_3COOH$) and 0.1 mol of sodium acetate ($CH_3COONa$) provides a buffer of pH = 4.74. Calculate the pH of solution after the addition of 0.02 mole of NaOH ($K_a = 1.8 \times 10^{-5}$).

(c) What is buffer and buffer capacity? Give Henderson equation for an acidic buffer.

(d) Give the pHmetric titration curve for weak acid and weak base titration. Explain why the titration of weak acid and weak base is not carried out volumetrically by using indicator.          (4,4,4,3)

3. (a) Write short note on **(any 2)**

   (i) Theory of acid base indicators and its use.

   (ii) Debye Huckel Onsager theory as applied to the variation of molar conductivity with dilution of a strong electrolyte.

   (iii) Quantitative relationship between Cp and temperature.

(b) A solution has 0.1 M in $Cl^-$, 0.1 M in $Br^-$ and 0.1 M in $I^-$. Solid $AgNO_3$ is gradually added to this solution. Assuming that the addition of $AgNO_3$ does not change volume. Answer the following :

     (i) What concentration of $Ag^+$ will be required to start the precipitation of each of the three ions?

     (ii) Which ion will precipitate first?

         Given   $Ksp\ (AgCl) = 1.7 \times 10^{-10}\ M^2$

                $Ksp\ (AgBr) = 5.0 \times 10^{-13} M^2$

                $Ksp\ (AgI) = 8.5 \times 10^{-17}\ M^2$

(c) Explain and derive the moving boundary method for the determination of transport number of ions.

(d) For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$

     Prove $K_p^0 = \dfrac{4\,(1-\alpha^2)}{3\sqrt{3}\,\alpha^2}\ \dfrac{P^0}{P}$           (4,4,4,3)

4.   (a) Explain : **(any 2)**

     (i) $NH_2^-$ and $NH_4^+$ have exceptionally high ionic conductivities in ammonia solution.

(ii) Transport number of chloride ion in aqueous 0.1 M HCl solution is lower than that in aqueous 0.1 MNaCl solution under identical conditions.

(iii) Conductivity increases with high frequency and high electric field.

(b) At 300K the molar conductance at infinite dilution of KCl, $KNO_3$ and $AgNO_3$ are $149.9 \times 10^{-4}\ \Omega\ m^2\ mol^{-1}$, $145.0 \times 10^{-4}\ \Omega\ m^2\ mol^{-1}$, $133.4 \times 10^{-4}\ \Omega\ m^2\ mol^{-1}$ respectively. Calculate molar conductance of AgCl at infinite dilution. If the conductivity of a saturated solution of AgCl at 300 K is 188.7 $\Omega^{-1}\ m^{-1}$, Calculate the solubility and solubility product of AgCl.

(c) Why conductometric titrations better than volumetric titrations. Sketch and explain conductometric titration curve of weak acid vs strong base titration.

(d) Give difference between electrolytic and metallic conductance. Give relation of equivalent conductivity and molar conductivity for $K_4[Fe\,(CN)_6]$ (4,4,4,3)

5. (a) How can the following properties be determined experimentally from conductance measurements:

    (i) Degree of hydrolysis and hydrolysis constant of hydrolysable salt

    (ii) Degree of ionization and ionic product of water.

  (b) In the determination of transport number of $Ag^+$ ions in a Hittorf's cell using Ag electrodes and $AgNO_3$ solution, it was found that 0.2157g of Ag was present in 24.96 g of water in the anode compartment after electrolysis. After electrolysis, 0.28 g of Ag was present is 27.8538 g of solution. A copper coulometer connected in series showed a deposit of 0.014 g of Cu. Calculate transport number of $Ag^+$.

  (c) What is the transport number of an ion. Derive the relation of transport number with ionic mobility and ionic conductance also.

  (d) State and explain the Faraday's Law of electrolysis.             (4,4,4,3)

6. (a) Explain the law of constancy of interfacial angles?

(b) An element (atomic mass = 60 amu) having face centred cubic unit cell has a density of 6.23 g/cm$^3$ Calculate the edge length of the unit cell?

(c) Describe investigation of internal structure of a solid by X-ray diffraction by using Bragg's method.

(d) A crystal plane has intercepts on the three axes of crystal in the ratio of 3:2:1. What are the miller indices of the plane? (4,4,4,3)

7. (a) Describe the structure of Cesium Chloride.

(b) What is meant by crystallographic axes and axial ratio?

(c) What is the radius ratio rule? How does co-ordinate number vary with the radius ratio rule?

(d) State three fundamental laws of Crystallography. (4,4,4,3)

8. (a) What is Le Chatelier's principle. State the effect of temperature, pressure and amount of reactant for the following equilibrium on the basis of Le Chatelier's principle qualitatively

$$PCl_5 \rightleftharpoons PCl_3 \text{ (g)} + Cl_2 \text{ (g)} \, \Delta H = -32.7 \text{ k Cal}$$
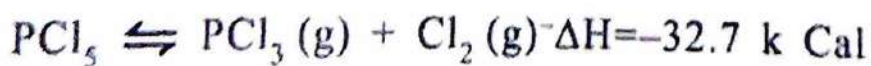
(b) (i) Derive thermodynamic expression for chemical equilibrium.

(ii) How are $K_p$, $K_c$ and $K_x$ related?

(c) "Equilibrium constant is a measure of free energy change." Explain and establish a relationship between them.

(d) Calculate $\Delta G°$ and $K_p$ for the following reaction at 298 K

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

Given that $\Delta G°$ for $CO(g)$, $CO_2(g)$ and $H_2O(g)$ are –32.807, –97.26 and –54.64 cal mol⁻¹ respectively.

(4,4,4,3)

(1500)

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

Sr. No. of Question Paper : 1670      **G**

Unique Paper Code     : 2173012005

Name of the Paper     : DSE: Solutions, Colligative Properties, Phase Equilibria and Adsorption

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

Semester             : III

Duration : 3 Hours          Maximum Marks : 90

## Instructions for Candidates

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

2. **All** questions carry equal marks.

3. Attempt **SIX** questions in all.

4. Use of Scientific calculators is allowed.

P.T.O.

1. Attempt any **five** (3 mark each) :

(a) Why does the plait point lie either to the right or to the left of the binodal curve?

(b) Explain whether the melting point of a solid substance will be raised or lowered by applying pressure if solid does not float on the liquid.

(c) What is the effect of pressure on the chemical potential versus temperature graph?

(d) What is the difference between Congruent and Incongruent melting compound?

(e) Salt is used to clear ice in sidewalks in winters. Explain.

(f) Show that it is not possible to have more than three phases in equilibrium with each other in a one component system.

(g) Discuss the factors which influence the adsorption of a gas on a solid.          (3×5)

2. (a) Why are the colligative properties of a solution containing an electrolyte different from those of a solution containing non-electrolyte of same concentration? What is the effect of dilution on colligative properties of solution containing a weak electrolyte? (5)

(b) Derive, thermodynamically, the relation $\Delta T_b = K_b \, m$. On what factors does $K_b$ depend? (5)

(c) The vapour pressure of a solution containing 6.7 g of $Mg(NO_3)_2$ dissolved in 100 g of water is 745 Torr at 373 K. Calculate the degree of dissociation of the salt in the solution. Molar mass of $Mg(NO_3)_2$ = 148.31 g mol$^{-1}$. (5)

3. (a) Define number average and mass average molar mass? Which of these is obtained by measurement of colligative properties? Which of the colligative properties is preferred for determination of molar mass of macromolecules like polymers and proteins?

P.T.O.

(b) Show that the relative lowering of vapour pressure of a solvent is equal to the mole fraction of the non-volatile solute and hence show that the relative lowering is a colligative property. Discuss how the relative lowering of vapour pressure for a dilute solution can be utilized in determining the molar mass of the solute. (5)

(c) The addition of 2.5 g of a substance to 100 g of $CCl_4$ raises the boiling point of $CCl_4$ by 0.50 K. Calculate the freezing point depression, the relative vapour pressure lowering, the osmotic pressure of the solution at 298 K, and the molar mass of the substance. The density of $CCl_4$ is 1.59 g cm$^{-3}$. Given: $K_b = 5.02$ K kg mol$^{-1}$, $K_f = 32$ K kg mol$^{-1}$. (5)

4. (a) Deduce the number of components and degrees of freedom for :

   (i) The system $NH_4Cl$ (s) – $NH_3$ (g) – HCl (g) in which $P_{NH3} = P_{HCl}$.

(ii) Liquid and its vapour in equilibrium with each other.      (5)

(b) Derive the phase rule for the non-reactive system, consisting of C components and P phases, when component, 2 and 3 are missing in phase 1.

      (5)

(c) What is the boiling point of water on a mountain where the barometric reading is 500 Torr? The enthalpy of vaporization of water may be taken as 2.259 kJg$^{-1}$.

      (5)

5. (a) Draw the temperature - composition diagram of a system exhibiting negative deviation from Raoult's law and explain the process of distillation of such a mixture.      (5)

(b) Derive Gibbs-Duhem-Margules equation starting from the Gibbs-Duhem equation for a system of two components.      (5)

(c) The system Pb (m. pt. 327°C) and Sb (m. pt. 631°C) exhibits a simple eutectic at 86% Pb (by mass) and 246°C. Breaks in the cooling curves in thermal analysis were found for the following compositions :

| T(°C) | 550 | 500 | 400 | 300 | 296 |
|---|---|---|---|---|---|
| Mass % Pb | 30 | 44 | 66 | 80 | 96 |

Draw a tentative phase diagram for the system and label it.

(5)

6. (a) State and derive Nernst distribution law. What are the limitations of the law?

(5)

(b) Experiments in the study of the distribution of phenol between water and chloroform gave the following result :

| Concentration in aqueous solution ($C_1$) | 0.094 | 0.163 | 0.254 | 0.436 |
|---|---|---|---|---|
| Concentration in Chloroform ($C_2$) | 0.254 | 0.761 | 1.850 | 5.430 |

What conclusion can you draw from these results concerning the molecular conditions of phenol in chloroform solution? (5)

(c) What is lever rule? Deduce it from pressure versus composition diagram for an ideal binary liquid mixture. (5)

7. (a) Differentiate between physisorption and chemisorption. 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.

| Gas | $O_2$ | $N_2$ | $H_2$ |
|---|---|---|---|
| $T_c$/K | 154 | 126 | 33 |

(b) Derive Langmuir adsorption equation. Explain how the variation of adsorption is accounted for at lower temperature, higher pressures and in the intermediate range of pressures.

(5)

(c) Write the expression for BET equation for adsorption. Draw and explain five different types of adsorption isotherms which are observed at high pressures.

(5)

8. Write short notes on the following : **(any three)**

(a) Zone Refining

(b) Acetic Acid-Chloroform-Water system

(c) Critical Solution Temperature

(d) Clausius- Clapeyron Equation

(e) Steam Distillation

(5×3)

(1000)

[This question paper contains 4 printed pages.]

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

Sr. No. of Question Paper : 4429　　　　　　　G

Unique Paper Code　　　: 32177901

Name of the Paper　　　: DSE: Novel Inorganic Solids

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

Semester　　　　　　　: V

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.

3. **All Questions carry equal marks.**

1. (a) Explain one dimensional metal by taking the example of oxidized tetracyanoplatinate(II) complex. What is the significance of Peierls distortion?

P.T.O.

(b) Discuss the working of Solid Oxide Fuel Cells (SOFCs). What are its benefits and drawbacks?

(c) What are condensates? What role do they play in *in-vitro* DNA synthesis control? $(5 \times 3 = 15)$

2. (a) Describe Topotaxy in context of nucleation of $MgAl_2O_4$ Spinel on: (a) $MgO$ & (b) $Al_2O_3$.

(b) What are nematic liquid crystals? Describe the various applications of inorganic liquid crystals.

(c) What are Single Molecular Magnets? Explain giving examples. $(5 \times 3 = 15)$

3. (a) Discuss the conduction mechanism of conducting polymer polyaniline (PANI). Also, give its applications.

(b) How does the structure of Zirconia, $ZrO_2$ supports it to function as a solid electrolyte? Discuss in detail. Why are cationic electrolytes more common than solid anionic electrolytes?

(c) State the law that relates the angles for the coherent scattering of waves from a crystalline solid. Explain how XRD helps in characterizing the nanoparticles. $(5 \times 3 = 15)$

4. (a) What are the differences between SEM and TEM techniques used for characterizing nanoparticles? Which one is more suitable for measuring the size and shape of nanoparticles, and why?

(b) Write a short note on Inorganic phosphors or Inorganic nanowires.

(c) What is the role of matrix and reinforcement in composite materials? Discuss the effect of the environment on various composite materials.

$$(5\times3=15)$$

5. (a) Explain how the hydrothermal method is used for the synthesis of synthetic emeralds. Give the schematic representation of an autoclave used for crystal growth. Also, give its limitations.

(b) What are refractories? Explain the different types of refractories and their applications.

(c) What are the different types of carbon nanotubes? Describe the Chemical Vapour Deposition (CVD) technique for the synthesis of carbon nanotubes.

$$(5\times3=15)$$

6. (a) Explain biomimetics with respect to artificial fossilization. Discuss the shell of Red Abalone, a natural composite.

P.T.O.

(b) Describe the reactions that occur during each step of the sol-gel synthesis of inorganic solids utilizing alkoxides as precursors.

(c) Titanium dioxide is used almost universally as a white pigment. Explain. $(5 \times 3 = 15)$

7. (a) What are ion-exchange resins? How do ion-exchange resins work?

(b) What are the two approaches for the synthesis of nanoparticles? Explain any one method for the synthesis of Gold nanoparticles in detail.

(c) Explain Quantum dots (QD) by giving examples. Compare the band energies for a quantum dot nanocrystal and a bulk semiconductor.
$(5 \times 3 = 15)$

[This question paper contains 8 printed pages.]

Sr. No. of Question Paper : **4544**          **G**

Unique Paper Code          : 32177903

Name of the Paper          : DSE-II Applications of Computers in Chemistry

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

Semester                   : V

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 only **Six** Questions in All.

3. Question Number **1** is compulsory. Attempt any **five** questions out of remaining **six** questions.

4. Attempt all parts of a question together.

5. Calculator is allowed.

P.T.O.

1. Attempt all the parts.

(a) Write the full form of the following abbreviations :

    (i) QBASIC

    (ii) PIXEL

    (iii) BCD

    (iv) IPO

(b) Write the following algebraic expressions in BASIC :

    (i) $C = 2 \pi r$

    (ii) $p = \dfrac{nRT}{V - nb} - \dfrac{an^2}{V^2}$

    (iii) $G° = -RT \ln Kc$

    (iv) $r = k(a - x)(b - x)^2$

(c) Identify and correct the incorrect numeric/string variables (IF ANY)?

    (i) REM

    (ii) L7

(iii) T6$

(iv) 8VOL!

(v) J*5

(vi) PI$

(vii) F4

(viii) XY%

(d) Explain the following terms :

(i) PRINT semi colon control and comma control statement

(ii) Debugging

(iii) RESTORE statement         (4,4,4,3)

2. (a) Write a program in BASIC to read and print the following matrix and then carry out the transpose of following matrix.

$$\begin{vmatrix} 4 & 7 & 9 \\ 2 & 8 & 6 \\ 1 & 3 & 5 \end{vmatrix}$$

(b) Convert the given numbers :

    (i) $(11001.11)_2$ to octal

    (ii) $(1432.46)_{16}$ to binary

(c) Write differences between BIT, BYTE and NIBBLE.

(d) Write a BASIC program

    where A$= "DECEMBER 08,2022", make use of string library functions RIGHT$, LEFT$, MID$ to print the output as 08 DECEMBER, 2022

                                              (3,3,3,3)

3. (a) Explain Regula Falsi Method. Give one example of its application in chemistry.

   (b) Debug the following Program and write the correct form

     SCREEN

     LOCATE 5,90

     PRINT IDEAL GAS ISOTHERM

     WINDOW (0,30)-0.5,400

```
FOR V=0.5 TO 0.05

P=0.082*T/x

PSET p, v

NEXT T

END
```

(c) Write a short note on machine language and assembly language.

(d) Write output of CINT (5.9) and FIX (5.9).

(3,4,3,2)

4. (a) Write a program in QBASIC to calculate the Mean and Standard Deviation for following observations obtained in the determination of metal ion concentration in industrial effluent sample:

0.142ppm, 0.171 ppm, 0.123ppm, 0.341 ppm, 0.161 ppm.

(b) Give the differences between PRINT TAB(X) and LOCATE command.

(c) Draw four concentric circle with origin at (125,95) in Screen 2.

P.T.O.

(d) Explain with example :

    (i) Syntax error

    (ii) Subscript out of range

    (iii) Type mismatch                 (4,2,3,3)

5. (a) Write the syntax of the following commands with one example

    (i) PSET

    (ii) LINE

(b) What is the difference between computer screen coordinates and world coordinates? Give the syntax for changing screen coordinates to world coordinates.

(c) Write a Program in QBASIC to find the value of $^nCr$ using GOSUB---RETURN statement.

(d) Name the INPUT and OUTPUT devices used in computers.                 (4,3,3,2)

6. (a) Differentiate between relational and logical operators.

(b) Write a program in QBASIC to determine the roots of the given equation using Iterative method, $x^3 + 8x^2 - 10 = 0$.

(c) Explain with examples the difference between USER DEFINED Functions and Library Functions in QBASIC.

(d) Write a program in QBASIC to calculate the sum of first 20 even numbers. (2,4,3,3)

7. (a) Write the BASIC statements to produce the following effects

    (i) Assign the value represented by the variable A to the variable B

    (ii) Reserve 9 spaces in a single array

    (iii) If variable y has value less than equal to 50 then transfer control to 80 otherwise execute next statement

    (iv) Find Cosine of angle C

(b) Illustrate the difference between INPUT and READ....DATA statement by giving examples.

(c) What is the speciality of WHILE...WEND statement? Explain.

(d) What is the purpose of VIEW command?

(4,3,3,2)

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

Sr. No. of Question Paper : 4806       G

Unique Paper Code     : 42174304

Name of the Paper     : Solutions, Phase Equilibria, Conductance, Electrochemistry & Functional Group Organic Chemistry-II

Name of the Course     : B.Sc. (Prog.)

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. **Section A** and **Section B** carry equal marks.

3. Use separate answer sheets for **Section A** and **Section B**.

4. Use of simple calculator is allowed.

P.T.O.

# SECTION A

*(Attempt any three questions in all)*

1. (a) Draw and discuss the phase diagram of water.

   (b) Explain the impact of impurities on the CST of phenol-water system.

   (c) Discuss the vapour pressure properties of two immiscible liquids. How are these facts utilized in determining molar mass of a liquid by steam distillation. (4,4,4.5)

2. (a) Explain how we determine transport number using Hittorf's method.

   (b) Plot well labelled conductometric titration curves obtained in the titration of

      (i) strong acid and strong base

      (ii) weak acid and strong base

State any two advantages of conductometric titration over volumetric titration using indicators.

(c) Specific conductance of 0.01M acetic acid solution at 25°C is $1.63 \times 10^{-2}$ $Sm^{-1}$ and its molar conductance at infinite dilution is $390.7 \times 10^{-4}$ $Sm^2 mole^{-1}$. Calculate the degree of dissociation and dissociation constant of the acid.

(4,4,4.5)

3. (a) Discuss the factors on which transport number depends.

(b) Explain why $KCl-NaCl-H_2O$ is a 3-component system whereas $KCl-NaBr-H_2O$ is a 4-component system.

(c) Calculate the equilibrium constant at 298K for the following reaction :

P.T.O.

$$Sn^{+2} + Fe^{+3} \rightleftharpoons Sn^{+4} + Fe^{+2}$$

(Given that $E^\circ(Fe^{+3}, Fe^{+2}) = +0.77V$ and $E^\circ(Sn^{+4}, Sn^{+2}) = +0.15V$)

(d) How does a salt bridge in galvanic cell prevent the liquid junction potential?                    (3,3,4,2.5)

4.    Write short notes on the following **(Any five)** :

(a) Concentration cells

(b) Differentiate between Congruent and incongruent melting compound system.

(c) Solvent extraction

(d) Lever rule

(e) Determination of Transport Number using Moving Boundary method.

(f) Ag-AgCl electrode                    (2.5×5=12.5)

## SECTION B

*(Attempt any **three** questions in all)*

5. (a) How will you distinguish between aniline N-methylaniline and N, N-dimethylaniline using nitrous acid? Give the reaction involved.

   (b) Describe Edman degradation method to determine the N-terminal amino acid in a peptide chain.

   (c) Explain the term isoelectric point and its application in the separation of amino acids.

   (d) How benzene diazonium chloride can be converted to (i) Benzene (ii) Phenol.      (3.5,3,3,2×1.5)

6. (a) Write the structure of products when D-glucose react with the following :

(i) Excess of $C_6H_5NHNH_2$

(ii) HI/Red Phosphorus

(iii) $Br_2$ water

(b) How will you convert an aldohexose to aldopentose sugar?

(c) The alkaline hydrolysis of an ester is preferred than acidic hydrolysis. Justify.

(d) Explain why direct nitration of aniline gives m-nitroaniline instead of o, p-products. How aniline can be converted into p-nitroaniline?

(3×1,3,3,3.5)

7.  (a) What are essential amino acids? How will you synthesize glycylalanine starting from glycine and alanine using N-protection and C-activating group.

(b) What happens when aqueous solution of $\alpha$-D-Glucose is kept for some time? Name the phenomenon and discuss the mechanism.

(c) Arrange the following in order of increasing basic strength and justify your answer :

(i) $CH_3CH_2NH_2$, $CH_3CONH_2$, $CH_3NHCH_3$

(ii) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $p\text{-}NO_2C_6H_4NH_2$

$$(4.5, 4, 2\times2)$$

8. (a) What are different methods used for estimation of amino acids in proteins?

(b) Write short notes on any **three** of the following :

(i) Claisen condensation

(ii) Schotten-Baumann Reaction

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

Sr. No. of Question Paper : 1754      **G**

Unique Paper Code     : 2172511101

Name of the Paper     : DSC – Basic Concepts of Organic Chemistry

Name of the Course    : B.Sc. (Prog.)

Semester     : I

Duration : 2 Hours          Maximum Marks : 60

## Instructions for Candidates

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

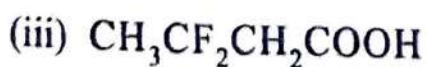2. Attempt any **four** questions.

3. All questions carry equal marks.

1. Attempt any five :

    (a) Giving reasons, arrange the following in increasing order of reactivity towards ring bromination :

P.T.O.
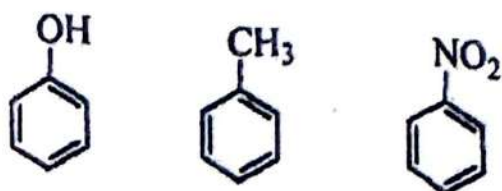
(b) What is Markownikoff's rule? Explain by taking the example of propene and HBr.

(c) Differentiate between D/L and d/1 notations.

(d) Explain, which of the following compound would be strongest acid?

   (i) $CHF_2CH_2CH_2COOH$

   (ii) $CH_3CH_2CF_2COOH$

   (iii) $CH_3CF_2CH_2COOH$

   (iv) $CH_3CH_2CH_2COOH$

(e) Amides are less basic than amines. Justify.

(f) Explain Hyperconjugation and its applications.

(g) What are free radicals? Explain decreasing order of stability of tertiary, Secondary, Primary alkyl free radical.                (3,3,3,3,3)

2.    (a) Draw the structure and explain, why chair form is the most stable form of cyclohexane?

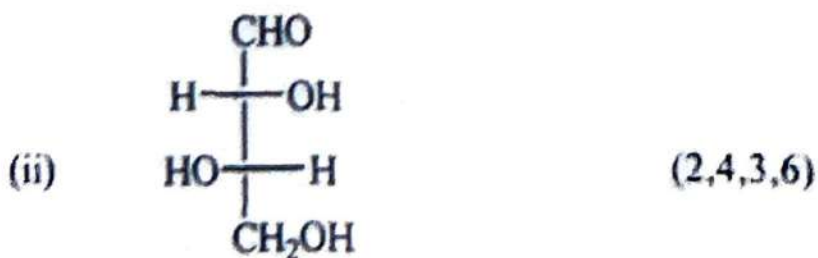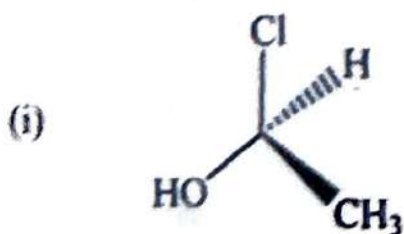(b) Assigning the priority order, explain how will you design at E/Z to the following :

(i)

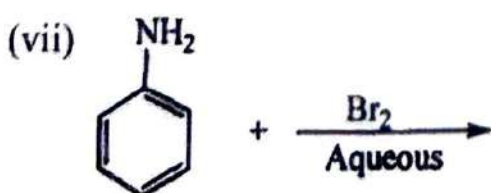(ii)

$$H_2N \quad CH_2Br$$
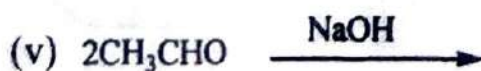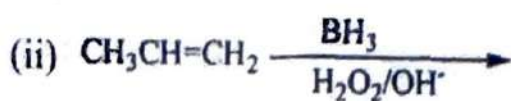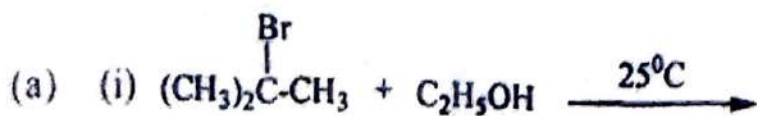$$C=C$$
$$H_3C \quad Cl$$
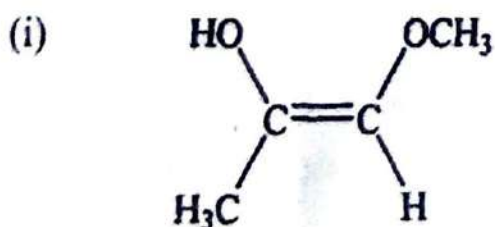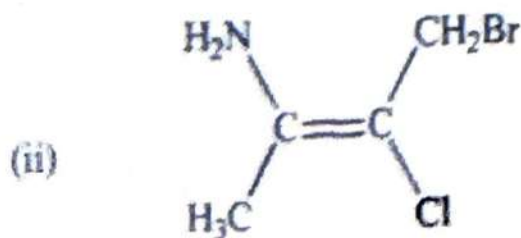
(c) What is the difference between meso stereoisomers and racemic mixture?

(d) Assigning the priority order and designate R/S to the following conformers :

(i)

$$
\begin{array}{c}
Cl \\
| \quad \cdots H \\
HO \quad CH_3
\end{array}
$$

(ii)

$$
\begin{array}{c}
CHO \\
H-\!\!-OH \\
HO-\!\!-H \\
CH_2OH
\end{array}
$$

(2,4,3,6)

3. Complete the following reactions **(any Six)** :

(a)    (i) $(CH_3)_2\overset{\overset{\displaystyle Br}{|}}{C}-CH_3$ + $C_2H_5OH$ $\xrightarrow{\;25^0C\;}$

     (ii) $CH_3CH=CH_2$ $\xrightarrow[\;H_2O_2/OH^-\;]{\;BH_3\;}$

     (iii) $C_6H_5CHO$ + $HCN$ $\longrightarrow$

     (iv) $CH_3CH_2MgBr$ + $CH_3COCH_3$ $\xrightarrow[\;H_2O\;]{\;Dry\;ether\;}$

     (v) $2CH_3CHO$ $\xrightarrow{\;NaOH\;}$

     (vi) $CH_3Cl$ + $AgCN$ $\longrightarrow$

     (vii)



$+$ $\xrightarrow[\;Aqueous\;]{\;Br_2\;}$

P.T.O.

(b) Arrange the following compounds in decreasing order of reactivity towards SN1 reactions and justify.

1-Bromopentane, Allyl bromide, Vinyl bromide.

(2,2,2,2,2,2,3)

4. (a) Discuss the mechanism of Friedel-Crafts acylation.

(b) Differentiate between Hoffman and Saytzeff elimination by taking the example of 2-Bromo butane.

(c) Give the mechanism of nitration of benzene. Explain why nitration of toluene is easier than that of benzene? (5,5,5)

5. Explain the following :

(a) Discuss the stereochemistry of the product of SN2 reaction.

(b) How can chlorobenzene be converted into aniline via benzyne mechanism?

(c) Write the mechanism of the reaction when two moles of aldehyde containing alpha hydrogen undergo condensation in the presence of a base. (5,5,5)

6. Write short note on **any three** of the following :

(a) Reimer-Tiemann Reaction

(b) Beckmann rearrangement

(c) Benzoin condensation

(d) Birch Reduction

(e) Pinacol-pinacolone rearrangement      (5,5,5)

(3000)

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

Sr. No. of Question Paper : 4950      **G**

Unique Paper Code : 42177925

Name of the Paper : DSE Chemistry of d-block Elements, Quantum Chemistry and Spectroscopy

Name of the Course : **B.Sc. Prog. / Analytical Chemistry / Industrial Chemistry**

Semester : V

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. Use separate answer sheets for **Section A** and **B**.

3. Attempt **three** questions from each section.

4. Each question carries equal marks.

5. Do not intermix the sections and attempt all parts of a question together.

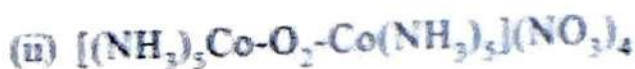6. Use of scientific calculator and logarithmic tables is allowed.
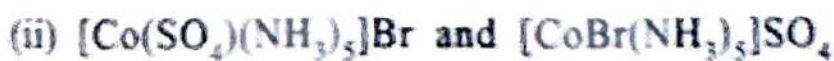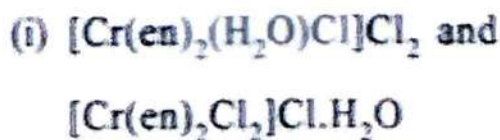
P.T.O.

## Section A

### (Inorganic Chemistry)

*Attempt any* three *questions.*

1. (a) Give the IUPAC names of any three complexes of the following :

   (i) $[Cr(NH_3)_6][Co(C_2O_4)_3]$

   (ii) $[(NH_3)_5Co-O_2-Co(NH_3)_5](NO_3)_4$

   (iii) $[Mo(N_3)(NH_3)_5](SO_4)_3$

   (iv) $[RhBrCl(en)_2]^+$

   (b) Name the type of isomerism in the following pairs and suggest a method to distinguish them :

   (i) $[Cr(en)_2(H_2O)Cl]Cl_2$ and $[Cr(en)_2Cl_2]Cl.H_2O$

   (ii) $[Co(SO_4)(NH_3)_5]Br$ and $[CoBr(NH_3)_5]SO_4$

(c) Give all possible stereoisomers (geometrical and optical isomers) for the following complexes :

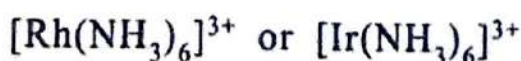$[Pt(en)_2Cl_2]Cl_2$; $[Cr(gly)_3]$ (6,3,3.5)
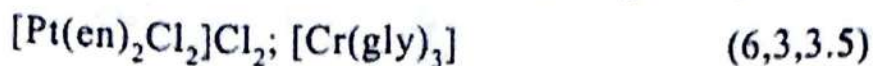
2. (a) Answer **any three** of the following :

(i) What is CFS? Define Crystal Filed Stabilization Energy (CFSE).

(ii) All the octahedral complexes of Ni(II) must be outer orbital complexes. Explain why?

(iii) Which of the following complexes amongst the following pairs, have high 10Dq value and why?

$[Rh(NH_3)_6]^{3+}$ or $[Ir(NH_3)_6]^{3+}$

(iv) Explain why $[CoCl_4]^2$ (blue) and $[Co(H_2O)_6]^{2+}$ (pink) have different colours. Which complex has its absorption bands at longer wavelength and why?

(b) Write the IUPAC formulae of **any two** of the following :

P.T.O.

(i) Sodium dithioscyanato(S)) argentate(I)

(ii) Potassium dicyanidobis(oxalato) nickelate(II)

(iii) Diamminebis(triethylphosphine)palladium(II) perchlorate

(c) State Jahn Teller theorem. Chromium(II) fluoride has a central metal ion surrounded by six fluoride ligands having two Cr-F bonds longer than the remaining four Cr-F bonds. Give reason for the observed distortion and also draw the crystal field splitting diagram. (6,3,3.5)

3. (a) Answer **any three** of the following :

(i) Transition elements can form complexes in zero or even negative oxidation states. Explain giving reasons.

(ii) The radii of the elements of third transition series are very similar to those of second transition series.

(iii) Explain the electronic spectra observed in Lanthanoids and actinoids. What are the main transitions involved.

(iv) Actinoids exhibit other than +3 oxidation states. Why.

(b) Write the complete electronic configuration for the following elements / ions. Calculate the number of unpaired electrons in each :

(i) Element with atomic number 76

(ii) Element with atomic number 107

(c) What is the difference between an inner orbital complex and an outer orbital complex? Discuss with one example each.                    (6,3,3.5)

4.   (a) Answer **any two** of the following :

(i) How does the crystal field theory interpret the colour and spectra of transition metal complexes? Explain giving examples.

(ii) In a square planar complex, the CFS of the d-orbital energies of a central ion decrease in the sequence: $d_{x2-y2} > d_{xy} > d_{z2} > d_{xz}, d_{yz}$. Explain the decreasing trend in energies.

(iii) For a metal ion having $d^6$ configuration in an octahedral complex, the magnitude of crystal field splitting is 32,200 $cm^{-1}$, and the electron-pairing energy is 17,600 $cm^{-1}$. Calculate the crystal field stabilization energy for both the spin states. Predict whether the complex will be high spin or low spin.

(b) Using the valence bond method, i) assign the valence shell electronic configuration to the central metal atom, ii) predict the type of hybridization involved, and iii) the magnetic moment (in Bohr magnetons) for the following complex : $[Cr(NO_2)_6]^{4-}$.

(c) The Latimer Diagram (the reduction potential diagram) for Cu in acid solution is :

$$Cu^{3+} \xrightarrow{\ +1.8\ } Cu^{2+} \xrightarrow{\ +0.15\ } Cu^{+} \xrightarrow{\ +0.50\ } Cu$$
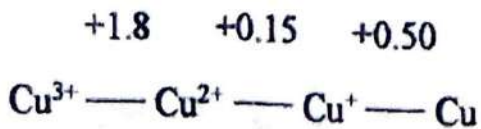
Based on the Latimer diagram :

(i) Which is the most stable species? Give reasons.

(ii) Calculate the skip step emf for the reduction of $CuO^{+}$ (i.e. $Cu^{3+}$) to $Cu^{+}$.

(iii) Which species of Cu is / are unstable with respect to disproportionation and why?

(6,3,3.5)

## Section B

### (Physical Chemistry)

*Attempt any* **three** *questions.*

**Physical Constants**

Planck's Constant $6.626 \times 10^{-34}$ Js

Avogadro's Number $6.023 \times 10^{23}$ mol$^{-1}$

Mass of electron $9.109 \times 10^{-31}$ kg

5. (a) What do you understand by an eigen value equation? Show which of the following mathematical functions are eigen functions of d/dx operator. Give the corresponding eigen values.

   (i) $5e^{3x}$

   (ii) $5 \cos 8x$

   (b) What is Grothus-Draper's law? A 0.04 M solution of a substance has an absorbance of 0.65 at 550 nm using a cell of path length 1 cm. Calculate molar extinction coefficient.

(c) What is the criteria for a molecule to be IR active? Based on this criterion, explain whether the following molecules are IR active or not and why?

   (i) $CS_2$

   (ii) $HCl$

   (iii) $N_2$

   (iv) $Br_2$? (4,4,4.5)

6. (a) Define Linear operator. If $\hat{A}$ & $\hat{B}$ are two operators show that :

   (i) $[\hat{A},[\hat{B},\hat{C}]] = \hat{A}[\hat{B},\hat{C}] - [\hat{B},\hat{C}]\hat{A}$

   (ii) $[\hat{A}^2,\hat{B}] = \hat{A}[\hat{A},\hat{B}] + [\hat{A},\hat{B}]\hat{A}$

(b) Determine the expectation value of kinetic energy for particle in a one dimensional box.

(c) What do you mean by quantum yield? Photobromination of cinnamic acid to dibromocinnamic acid was carried in blue light at the wavelength of 430nm, at 300K using the light intensity of $1.7 \times 10^{-3}$ J per second. An exposure of 25 minutes produced a decrease of 0.082 millimole of bromine. The solution absorbed 85% of the light passing through it. Calculate the quantum yield of the reaction.                    (4,4,4.5)

7.  (a) An electron is confined in a one dimensional box of length $10^{-9}$ m.

    (i) What is the energy of the electron in n = 1 level?

(ii) Calculate the energy absorbed when electron undergoes transition from $E_5$ to $E_6$ and $E_6$ to $E_7$.

(b) With the help of Jablonski Diagram, explain briefly the various types of radiative and non- radiative transitions.

(c) The force constant of $^1H\ ^{35}Cl$ molecule is 950 $Nm^{-1}$. Calculate the fundamental vibrational frequency as well as the zero-point energy. The atomic masses are: $H = 1.673 \times 10^{-27}$ kg; $Cl = 58.06 \times 10^{-27}$ kg. (4,4,4.5)

8. (a) Write short notes on **any two** of the following :

(i) Phosphorescence with diagram

(ii) Significance of $\psi$ and $\psi^2$

(iii) Selection Rules for Rotational spectra

P.T.O.

(b) What are the assumptions of the free electron model for polyenes. With the help of this model determine the energy for the first excited state of hexatriene molecule. Given that C-C bond length is 135 pm & that of C=C is 154 pm. Radius of carbon atom at the end is 77 pm.

(8,4.5)