SET A

[This question paper contains 3 printed pages]

Sr. No. of Question paper   **Roll No……………**

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

Semester   : II

Name of the Paper   : Organic Chemistry I: Basics and Hydrocarbons

Unique Paper Code   : 32171201

Duration   : 2 Hours

Maximum Marks   : 75 Marks

Instructions for students-

1. Attempt the paper on white plain sheet only.
2. Each sheet is to be numbered at the top.
3. Answer four questions in all.
4. All questions carry equal marks.

Q.1 (a) Draw all conformations of cyclohexane. Which conformation is more stable and why? Draw potential energy diagramme for the same.

(b) An optically active hydrocarbon "X" with M.F C_6H_{12} decolorises bromine solution in CCl_4. Compound "X" on reaction with mercuric acetate in presence of water in THF followed by reduction with sodium borohydride gives alcohol "Y" having M.F $C_6H_{14}O$. Compound "X" on oxidation with hot alkaline solution $KMnO_4$ gives carboxylic acid "Z" with M.F. $C_5H_{10}O_2$. Write down all the reactions involved with structure of X, Y and Z. Are "Y" and "Z" optically active or not?
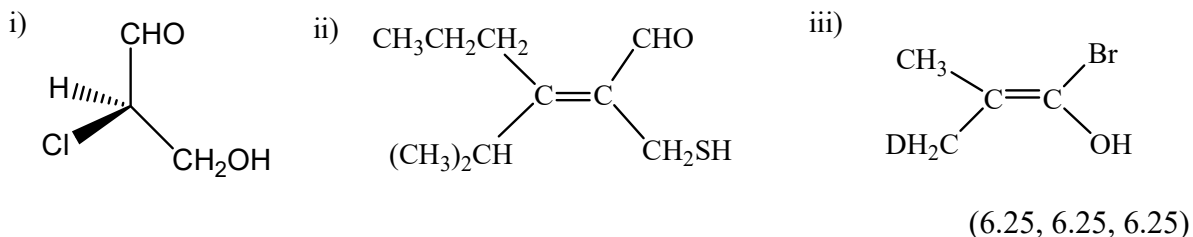
(c) How many monobrominated products are formed when isopentane is photobrominated? Also calculate the proportion of isomers formed. Relative reactivity of different types of hydrogens towards bromination is $3° : 2° : 1° = 1600 : 82 : 1$.

(6.25, 6.25, 6.25)

Q.2 (a) Write down the mechanism for hydration of propyne, when it is treated with aqueous sulphuric acid in presence of mercuric sulphate.

(b) Explain why 3,3-dimethyl-1-butene, when treated with HI, gives a mixture of two iodoalkanes. Write down the products formed and also designate them as major and minor.

(c) Assign E/Z or R/S configuration to following:

i)

CHO
H⳽⳽⳽ (wedge)
Cl
CH₂OH

ii) $CH_3CH_2CH_2$, CHO
$C=C$
$(CH_3)_2CH$, CH_2SH

iii)

CH_3 , Br
$C=C$
DH_2C , OH

(6.25, 6.25, 6.25)

Q.3 (a) Carry out the following conversions (any four)

    i. Ethylene glycol from ethane
    ii. Methylcyclopropane from isopropyl alcohol
    iii. 2-Pentyne from propene
    iv. Cis -2-butene from propyne
    v. p-Nitrostyrene from benzene

(b) Write down the products of Diel's Alder Reaction of 1,3-butadiene with i) fumaric acid ii) maleic anhydride (4 x 4 =16, 2.75)

Q.4 (a) Write down the product/s obtained when propene is treated with bromine in presence of aqueous solution of sodium iodide.

(b) Draw all possible stereoisomers for 1,3-dibromo-2-methylbutane. Comment upon their optical activity. Assign R/S configuration to any one of them.

(c) Explain why when benzene is treated with isobutylchloride in presence of anhydrous AlCl₃, it does not give isobutylbenzene. Give suitable method to synthesize isobutylbenzene.

(6.25, 6.25, 6.25)

Q.5 (a) What happens when isobutylene is treated with hydrogen bromide in presence of peroxide? Explain with mechanism.

(b) In 1,3-butadiene, 1,4-addition occurs slower than 1,2-addition at low temperature. Explain.

(c) Convert the following into Fischer Projection

(i)

OMe
H₃C , H
H , COOH
OAc

(ii)

COOH
Cl , H
Cl , H
Ph
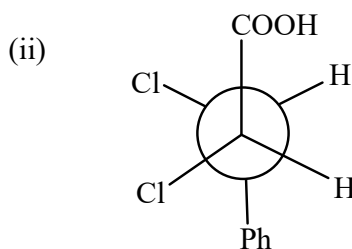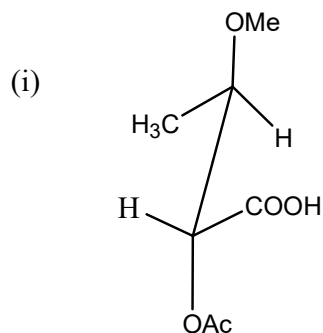
(6.25, 6.25, 6.25)

Q.6 Write down short note on (any three)

   i. Resolution of racemic mixture by diastereoisomeric salt formation method
  ii. Hoffman's elimination
 iii. Hyperconjugation
 iv. Stability of carbocation

(6.25, 6.25, 6.25)

Sr. No. of question Paper:

Unique Paper Code : **32171403**

Name of the Paper : Physical Chemistry - IV

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

Semester : IV

Time: 2 hours   Maximum marks: 75

Instructions for the candidates

1. Attempt any **Four** questions in all.
2. Each question carries equal marks.
3. Use of scientific calculator is permitted.

Q. 1. (a) What is zero order reaction? Give two examples. 6.75
Derive an expression for the rate constant and half-life period of a zero-order reaction using integrated rate law. What type of plots will you get for a zero order reaction for
(i) Concentration versus time
(ii) Half-life period versus initial concentration?

(b) For a first order opposed by first order reaction 6

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$
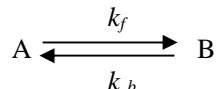
with the initial concentrations of A and B as $[A]_O$ and zero respectively, show that the integrated rate expression is given by

$$ln\left(\frac{x_{eq}}{x_{eq}-x}\right) = \left(k_f + k_b\right)t$$

where x is the concentration of B at time t and x_{eq} is the concentration at equilibrium.

(c) The rate constant of a first order decomposition of ethylene oxide into CH_4 and CO 6
follows the equation:
$$\log k \text{ (in s}^{-1}) = 12.34 - (1.25 \times 10^4)/T$$
Calculate:
(i) the activation energy of the reaction
(ii) the rate constant at 625 K and
(iii) the frequency factor, A

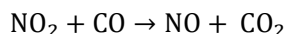Q.2. (a) The following mechanism has been proposed for the enzyme catalysis: 6.75

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} P + E$$
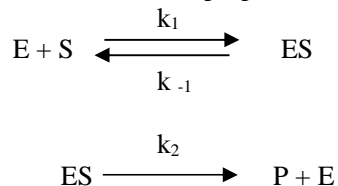
Show that the reaction rate is given by:

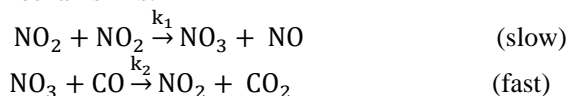$$\frac{d\,[product]}{dt} = \frac{K_2[E]_0\,[S]_0}{K_m + [S]_0}$$

Discuss the rate when $K_m \gg [S]_0$ and $K_m \ll [S]_0$.
Under what conditions will the order of the reaction be equal to one?

(b) Using Steady State Approximation, derive the differential rate law for the reaction   6
between NO_2 and CO at low temperature.

$$NO_2 + CO \rightarrow NO + CO_2$$

The proposed reaction mechanism is:

$$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \qquad \text{(slow)}$$
$$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2 \qquad \text{(fast)}$$

(c) The following data were obtained at a constant volume for the decomposition of di-   6
tertiarybutyl peroxide in the gas phase at427.7 K.

t/min	0	3	6	9	12	15	18	21
p/torr	169.3	189.2	207.1	224.4	240.2	255.0	269.7	282.6

The reaction is

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2\ CH_3COCH_3 + C_2H_6$$
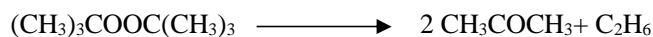
Show that the reaction is of first order and calculate its rate constant.

Q.3. (a) Discuss the asymmetry effect and electrophoretic effect in Debye Huckel Onsager theory   6.75

(b) Discuss the titration curves obtained in the conductometric titrations of: 6
(a) HCl versus NaOH solutions
(b) CH_3COOH versus NaOH solutions

(c) Calculate the transport numbers of H^+ ion and Cl^- ion from the following data obtained   6
from the moving boundary method using cadmium chloride as the indicator electrolyte.
(Given: Atomic weight of Ag = 108 g mol^{-1})

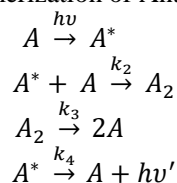|	
Concentration of HCl solution	= 0.100 N
Mass of silver deposited in the coulometer	= 0.1209 g
Movement of the boundary	= 7.50 cm
Cross – section of the tube	= 1.24 cm^2

Q.4. (a) Define ionic mobility and show that, the ionic mobility of a solution at infinite dilution is given by   6.75

$$\mu_+^\infty = \frac{\lambda_+^\infty}{z_+ F} \quad and \quad \mu_-^\infty = \frac{\lambda_-^\infty}{z_- F}$$

where the symbols have their usual significance.

(b) Define Molar Conductance and Equivalent Conductance. What are their units?   6
Explain the nature of variation of conductivity and molar conductivity with concentration both for weak and strong electrolytes.

(c) When a certain conductance cell was filled with 0.02 M KCl (with specific conductance   6
0.002768 ohm^{-1} cm^{-1}) it had a resistance of 82.4 ohms at 25 °C. When filled with 0.05 N K$_2$SO$_4$ it had a resistance of 326 ohm
Calculate the
   (i)   cell constant
   (ii)   conductance
   (iii)   specific conductance of 0.05 N K$_2$SO$_4$
   (iv)   equivalent conductance of 0.05 N K$_2$SO$_4$

Q.5 (a) The mechanism of photochemical dimerization of Anthracene (A) is given below: 6.75

$$A \overset{h\upsilon}{\rightarrow} A^*$$
$$A^* + A \overset{k_2}{\rightarrow} A_2$$
$$A_2 \overset{k_3}{\rightarrow} 2A$$
$$A^* \overset{k_4}{\rightarrow} A + h\upsilon'$$

Derive the expression for the rate of formation of dimer, A_2.
Show that the dimer concentration is independent of the monomer concentration at the photostationary state.

(b) State and derive Lambert Beer's law.   6

(c) In the photochemical reaction between Cl$_2$ and H$_2$, 2.5 x 10^{-10} moles of chlorine have been   6
converted to hydrochloric acid by irradiation with light of 4500 A°. What is the quantum efficiency if the light absorbed in the system is 30 x 10^{-15} J.

6 (a) Define quantum efficiency.   6.75
What are the reasons for low and high quantum efficiency of a photochemical reaction?

(b) A second order reaction in which the initial concentration of both the reactants are same   6
is 25% complete in 600 s. How long will it take for the reaction to go to 75% completion?

(c) Explain how the hydrolysis constant and degree of hydrolysis of a salt can be   6
determined using conductance measurements.

[This question papers contains   printed pages]

Roll No......................

Unique Paper Code   : 32177908
Name of the Paper   : Green Chemistry
Name of the course   : BSc (H) Chemistry
Semester   : VI
Duration   : 2 hrs
Maximum Marks   : 75

Instructions for Candidates:
1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **any** *four* questions.
3. Each question carries 18.75 marks.
4. Attempt all parts of a question together.
Take molecular mass of C = 12, N = 14, O = 16, S = 32, H = 1

1. (a) Fill in the blanks with the appropriate word(s):
    (i)   _____ is often referred to as universal green solvent.
    (ii)   The use of biodiesel is covered within Green Chemistry Principle number 7, which is _____.
    (iii)   _____ is a chemical responsible for the depletion of the ozone layer.
    (iv)   _____ is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs.
    (v)   _____ is referred to as the Father of Green Chemistry.
    (vi)   The atom economy of a rearrangement reaction is _____.
    (vii)   A cheap, readily available and non-polluting source of energy is _____.
    (b) List any four goals of green chemistry.
    (c) Use of catalytic reagents should be preferred compared to stoichiometric reagents. Justify the above statement.
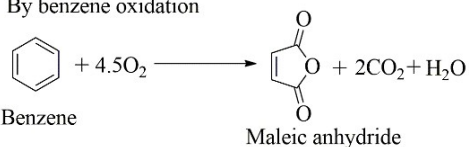   (7 X 1.5, 4, 4.25)

2. (a) Correct the following statements:
    (i) The first listed of the 12 Principles of Green Chemistry is use of benign solvents.
    (ii) Versatile organic compounds, VOCs, such as formaldehyde, have been replaced and banned in paints.
    (iii)Potato, corn and molasses are examples of non-renewable feedstocks.
    (iv)Carbon monoxide is an excellent green solvent and a common greenhouse gas.
    (v) Green Chemistry is also known as user friendly chemistry.
    (vi)Substitution reactions have the highest atom economy.
    (vii) Benzene is a safe and important industrial solvent.
    (b) With the help of a suitable example, explain one type of a reaction which provides highest atom economy.
    (c) Explain the different terms used in the Pollution Prevention Act of 1990 by US EPA: Risk = f (hazard × exposure)
    (7 X 1.5, 4, 4.25)

3. (a) Which is a greener route towards preparation of maleic anhydride? Justify.

Route-1

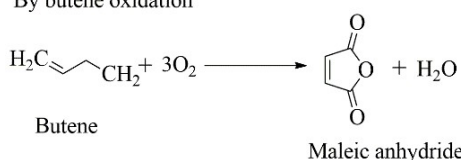By benzene oxidation

Benzene   Maleic anhydride

$+ 4.5O_2 \longrightarrow$ [maleic anhydride structure] $+ 2CO_2 + H_2O$

Route-2

By butene oxidation

$H_2C{\sim}\!\!\diagup\!{}_{CH_2} + 3O_2 \longrightarrow$ [maleic anhydride structure] $+ H_2O$

Butene

Maleic anhydride

(b) Provide one example of the following:
   (i) Persistent chemical
   (ii) Bio-catalyst
   (iii) Auxilliary Substance
   (iv) Toxic solvent commonly used by the dry cleaning industry
   (v) Ionic liquid
   (vi) Toxic antifouling agent
   (vii) phase transfer catalyst

(c) Write the reaction for the synthesis of the azomethine formed by the reaction of *ortho*-vanillin with *para*-toluidine. What are two advantages of performing a solventless reaction?

(4, 7 X 1.5, 4.25)

4. (a) Provide an example of the following types of reaction carried out under microwave conditions: (Any *two*)
   (i) Hofmann Elimination
   (ii) Diels-Alder reaction
   (iii) Hydrolysis of esters

(b) Provide the green method of synthesis: (Any *two*)
   (i) Poly lactic acid
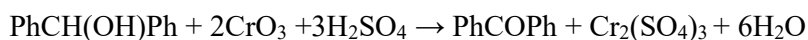   (ii) Disodium iminodiacetate (DSIDA)
   (iii) Adipic acid

(c) What are antifouling agents? Name and draw the structure of an environmentally friendly antifouling agent.
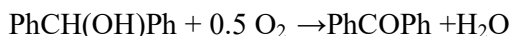
(7, 7, 4.75)

5. (a) Outline the green route towards the synthesis of the pesticide, Carbaryl. Which principle(s) of Green Chemistry is/are involved in this route?

(b) What do you understand by the term "Green Solvent"?Which green solvent is now used by dry cleaning industry?Listfour of its advantages over traditional organic solvents?

(c) Which is the preferred route to synthesize the acetophenone? Justify.

$$PhCH(OH)Ph + 2CrO_3 + 3H_2SO_4 \rightarrow PhCOPh + Cr_2(SO_4)_3 + 6H_2O$$

OR

$$PhCH(OH)Ph + 0.5\,O_2 \rightarrow PhCOPh + H_2O$$

6. Briefly discuss the role of the following in Green Chemistry (Any *three*):
   (i) Ultrasound assisted reactions
   (ii) Sustainable development
   (iii) Enzymatic Inter esterification for the production of non-trans fats and oils
   (iv) Careful use of blocking/protecting groups

(3 X 6.25)

Serial No. of Question Paper:

Unique Paper Code   : 32175916

Name of the Paper   : Chemistry of d-block elements, Quantum chemistry and Spectroscopy

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

Semester   : IV

Duration   : 2 hours

Maximum Marks   : 75

Instructions for candidates

1. Write your roll no. on the top immediately on receipt of this question paper.
2. Attempt **two questions** from **Section A** and **two** from **Section B.**
3. **Section A** and **B** are to be attempted separately in the same answer sheet.
4. Do not intermix the sections and attempt all parts of a question together.
5. Use of scientific calculator and logarithmic tables is allowed.

Section A

*Attempt **any two** questions*

1. (a) Give reasons for **any four** of the following:

     (i)   Aqueous solution of copper (II) ion is blue while Cu(I) salts are white.

     (ii)   UV-visible absorption bands of transition metal ions are broad whereas those of f-block elements are sharp

     (iii)   Crystal field splitting in tetrahedral complexes is less than the corresponding octahedral complexes

     (iv) Eu^{2+} acts as good reducing agent

     (v) $[Co(NH_3)_6]^{3+}$ is inner orbital octahedral complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital octahedral complex

     (b) Name the type of the isomerism exhibited by the complex $Na_3[Cr(SCN)_6]$. Also mention the names of the isomeric forms of the complex

     (c) Give the IUPAC names of any **three** complexes of the following:

         (i) $[PtCl_2(C_2H_4)(NH_3)]$

         (ii) $(CH_3)_4N[Cr(NH_2)_2Cl_2(NH_3)_2]$

         (iii) $[Cr(ONO)(NH_3)Br_2H_2O]$

         (iv) $[NH_3)_2Cl_2 Co-NH_2-O_2-Co NH_3)_2Cl_2]Cl_2$

2. (a) Crystal field splitting are listed in the following table for three complexes of iron. Explain the differences in values

Complex	(cm^{-1})
$[FeF_6]^{3-}$	15,000
$[Fe(CN)_6]^{3-}$	26,600
$[FeF_6]^{4-}$	22,000

   (b) Explain the method and principle behind ion exchange process for separation of lanthanides

   (c) Draw the crystal field splitting diagram for octahedral complex for d4 metal ion both in high spin and low spin state. For the complex ion $[Mn(H_2O)_6]^{3+}$, given mean pairing energy $P = 28,000 cm^{1-}$ and magnitude of Δ_0 is $21,000 cm^{-1}$, calculate CFSE corresponding to high spin and low spin states. In which of the states the complex is more stable

6.25, 6.25, 6.25

3. (a) Compare the behaviour/property for the given compounds/complexes. Explain the reasons for your choice:

   (i) Higher value of Δ_o $[Fe(CN)_6]^{3-}$ or $[Fe(H_2O)_6]^{3+}$

   (ii) Square planar geometry $[Ni(CO)_4]$ or $[Ni(CN)_4]^{2-}$

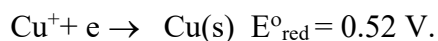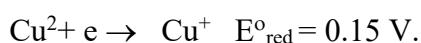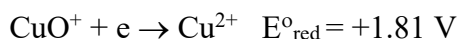   (iii) Anomalous electronic configuration- Cr   or   Mn

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

   (i)   Oxalatotetraaquairon(III)sulphate

   (ii)   Pentaamminehydroxidocobalt(III)chloride

   (iii)   μ-imido-μ-hydroxidobis[tetraamminecobalt(II)ion]

   (c) Construct the Latimer diagram for copper in acidic medium. Given below are the standard reduction potentials in volts at 25°C

$$CuO^+ + e \rightarrow Cu^{2+} \quad E°_{red} = +1.81 \text{ V}$$
$$Cu^2+ e \rightarrow Cu^+ \quad E°_{red} = 0.15 \text{ V}.$$
$$Cu^+ + e \rightarrow Cu(s) \quad E°_{red} = 0.52 \text{ V}.$$

   (i) Calculate skip step potential for CuO^+/Cu^+.

   (ii) Is there any species which undergoes disproportionation? If yes then why?

9, 4, 5.75

Section B

Physical Constants

Planck's constant 6.626×10^{-34} Js

Velocity of light 3.0×10^8 m s^{-1}

Avagadro's Number 6.023×10^{23} mol^{-1}

Mass of electron 9.1×10^{-31} kg

Boltzmann constant 1.38×10^{-23} J K^{-1}

*Attempt **any two** questions*

1. (a) Identify which of the following functions are eigenfunctions of the operator d^2/dx^2:
   (i) kx, (ii) $\cos kx$, (iii), (iv) $e^{-\alpha x^2}$. Give the corresponding eigenvalue where appropriate.

   (b) Calculate the probability that a particle will be found between 0.65L and 0.67L in a one dimensional box of length L when it has n = 1.

   (c) Determine whether or not the operators $\hat{x}$ and $\hat{p}_x$ commute. What is the physical significance if the two quantum mechanical operators commute with one another?

   6.25, 6.25, 6.25

2. (a) Convert the following spectroscopic quantities as indicated:
   (i) 1000 cm^{-1} to μm
   (ii) 0.15 nm to Hz
   (iii) 3500 cm^{-1} to J
   (iv) 9 GHz to cm^{-1}

   OR

   Calculate the wavelength for a transition between neighboring energy levels of a simple harmonic oscillator consisting of a particle of mass 5.16 x 10^{+24} kg and force constant 285 Nm^{-1}.

   (b) Differentiate between
   (i) primary and secondary processes
   (ii) probability and probability density

   (c) The pure rotational spectrum of the gaseous molecule CN has a series of equally spaced lines separated by 3.79 cm^{-1}. Calculate the internuclear distance of the molecule. The molar mass of C and N are 12.011 and 14.007 g mol^{-1} respectively.

   6.25, 6.25, 6.25

3. (a) What do you mean by normalization of wave function? Normalize the wave function $\psi = x(a-x)$ over the interval $0 \le x \le a$

   (b) Define Lambert-Beer's law. What are its limitations? Does it hold good in a concentrated solution of a light absorbing substance? Give reason.

   (c) What are the selection rules for molecule to be microwave active? What is the effect on the microwave spectrum of $^1H^{35}Cl$ if ^{35}Cl is substituted by ^{37}Cl? Explain.

   6.25, 6.25, 6.25

Unique Paper Code   :   42171205

Name of the Paper   :   Chemical Energetics Equilibria & Functional Group

                                      Organic Chemistry -I

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

Semester   :   II

Duration   :   2 Hours

Maximum Marks   :   75

Instructions for Candidates

1. Use Separate answer sheets for Sections A and B.
2. Use of Scientific Calculator is permitted.

SECTION A

(Physical Chemistry)

Attempt any **two** questions.

All questions carry equal marks.

1.   (a) What is a buffer solution? Give one example of acidic buffer and basic buffer solution. Explain how a buffer solution resists change in its pH.

(b) Show that the degree of hydrolysis of a salt of weak acid and weak base is independent of the concentration of the solution and derive the following equation

$$pH = -\frac{1}{2}[\log K_a + \log K_W - \log K_b]$$

(c) Determine the pH of a solution obtained by mixing equal volume of 0.1 M ammonium nitrate and 0.02 M ammonium hydroxide, K_b for NH_4OH being 1.8×10^{-5}.

(d) Derive relation of absolute entropy of substance and show that
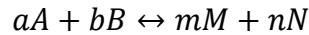
$$S_T = 2.303 \int_0^T C_p d \log T$$

$5, 5, 5, 3\frac{3}{4}$

2.   (a) For the chemical reaction

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) + Heat$$

(i) Write the expression for equilibrium constant K_P and

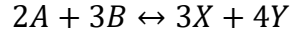(ii) Predict the effect of changes in temperature and pressure on equilibrium mixture.

(b) Derive the expression for the Van't Hoff reaction isotherm for the reaction
$$aA + bB \leftrightarrow mM + nN$$
Show that
$$\Delta G° = -2.303 \, RT \log K_P$$
(c) At 400K for the gaseous reaction
$$2A + 3B \leftrightarrow 3X + 4Y$$
The value of K_P is 0.05. Calculate the value of K_C.
(d) What is residual entropy? Calculate the entropy change accompanying the conversion of 1 mole of ice at 273.1 K into steam at 373.1 K under standard condition. Given that,
$$\Delta H_{fus} = + 6.00 KJ/mol$$
$$\Delta H_{Vap} = + 40.60 KJ/mol$$

$$5, 5, 5, 3\frac{3}{4}$$

3.   (a) Show that
$$\Delta H_1 - \Delta H_2 = \Delta C_P(T_2 - T_1)$$
(b) What is bond enthalpy? The bond enthalpies for (C=C), (C-C) and (C-H) bonds are 615.20, 347.77 and 413.478 KJ/mol. Calculate the enthalpy of formation of benzene on the basis of Kekule structure of benzene.
(c) Find out the bond enthalpy of C-H bond from the following data:
$$\Delta H_{f(CH_4)}° = -74.9 \, KJ/mol$$
$$\Delta H_{H-H} = 435.1 \, KJ/mol$$
and heat of sublimation of graphite is
$$C(s) \rightarrow C(g) \Delta H_{Sub} = 719.6 \, KJ/mol$$
(d) Define the terms enthalpy of solution and enthalpy of hydration.
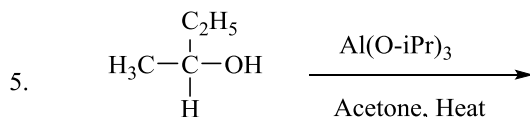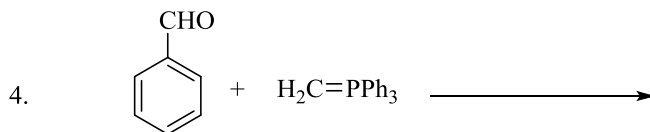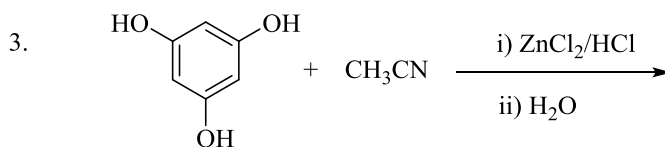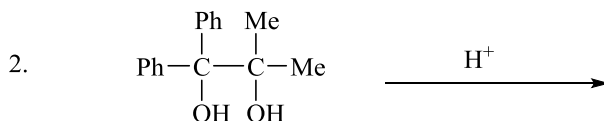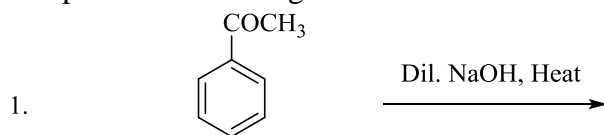
$$5, 5, 5, 3\frac{3}{4}$$

SECTION B

(Organic Chemistry)

Attempt any **two** questions.

All questions carry equal marks.

1.   (a) Why cyanide ion (CN⁻) is highly specific base in benzoin condensation. Explain with the help of mechanism.
      (b) Complete the following reactions and mention the name of the reaction:

1.
$$\overset{COCH_3}{\underset{}{\bigcirc}} \quad \xrightarrow{\text{Dil. NaOH, Heat}}$$

2.
$$\underset{\underset{OH\ \ OH}{|\ \ \ \ |}}{\overset{\overset{Ph\ \ Me}{|\ \ \ \ |}}{Ph-C-C-Me}} \quad \xrightarrow{H^+}$$

3.
$$\underset{OH}{\overset{HO\qquad OH}{\bigcirc}} \quad + \quad CH_3CN \quad \xrightarrow[\text{ii) } H_2O]{\text{i) } ZnCl_2/HCl}$$

4.
$$\overset{CHO}{\underset{}{\bigcirc}} \quad + \quad H_2C{=}PPh_3 \quad \longrightarrow$$

5.
$$\underset{\underset{H}{|}}{\overset{\overset{C_2H_5}{|}}{H_3C-C-OH}} \quad \xrightarrow[\text{Acetone, Heat}]{Al(O\text{-}iPr)_3}$$

      (c) Suggest the mechanism involved in the nitration of benzene *via* electrophilic substitution reaction.

$$5, 10, 3\frac{3}{4}$$

2.   (a) *o*-Chloroanisole and *m*-chloroanisole gives the common product with $NaNH_2$ and Liq. NH_3. Explain.
      (b) Write the structure of the compound **A**, **B**, **C** and **D**. Give the mechanism for the formation of compound **C** and **D** from **B**.

$$\text{C}_6\text{H}_6 \ + \ H_3C-\underset{\underset{H}{|}}{C}=CH_2 \quad \xrightarrow[250^oC]{H_3PO_4} \quad \textbf{A} \ \xrightarrow{O_2} \ \textbf{B}$$

$$\textbf{B} \ \xrightarrow{H^+/H_2O} \ \textbf{C} \ + \ \textbf{D}$$

(c) Identify the products and suggest the mechanism for the following reactions:

1. $\quad$ C$_6$H$_6$ $\quad$ + $\quad$ $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Cl$ $\quad \xrightarrow{\text{Anhyd. AlCl}_3}$

2. $\quad$ $Me-\underset{\underset{OH}{|}}{\overset{\overset{Me}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{Me}{|}}{C}}-H$ $\quad \xrightarrow{\text{Pb(OAc)}_4}$

(d) Arrange the following halides in the decreasing order of alkaline hydrolysis towards S_N1 reaction:

$\qquad$ (a) Ph_3CCl $\quad$ (b) CH_3Cl $\quad$ (c) $PhCH_2Cl$ $\quad$ (d) Ph_2CHCl

$$5, 5, 5, 3\frac{3}{4}$$

3. $\qquad$ (a) An organic compound "**A**" with molecular formula C_2H_4O, forms ppt. with 2,4-DNP. Compound "**A**" on heating with iodine in presence of sodium hydroxide gives yellow ppt of compound "**B**" on reaction of "**A**" with dilute NaOH, compound "**C**" is obtained which loses water molecule to form 2-butenal.

$\qquad$ (i) Identify **A**, **B**, **C,** explaining reaction involved.

$\qquad$ (ii) Write down the mechanism for the conversion of **A** to **C** conversion.

(b) The reactivity of aryl halides increases towards nucleophilic substitution reaction with substitution of -NO_2 group at o and p-positions. Explain.

(c) Explain giving reasons:

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

(ii) $S_N{}^2$ reaction of alkyl halides are accompanied by inversion of configuration.

(d) Arrange the following in increasing order of acidic strength. Give reasons for your answer:

(a) p-Nitrophenol $\qquad\qquad\qquad$ (c) o-Nitrophenol

(b) 2, 4, 6-Trinitrophenol $\qquad\qquad$ (d) Phenol

$$5, 5, 5, 3\frac{3}{4}$$

[This question paper contains 3 printed pages.]

Unique Paper Code   :   **42174404**

Name of the Paper   :   Chemistry of s and p Block Elements, States of Matter
                                                    and Chemical Kinetics

Name of the Course   :   **B.Sc. (P)**

Semester   :   IV

Duration   :   2 Hours

Maximum Marks   :   75

<u>Instructions for the Candidates</u>

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Use of Scientific calculators and log tables is allowed.
3. Use Separate sheets for **Section A** and **Section B.**

SECTION A

(INORGANIC CHEMISTRY)

Attempt any two questions

Question No. 1 is compulsory

1. (a) Give the structures and oxidation state of the central atom of any ***three*** of the following:

> (i) P_4O_{10}
>
> (ii) NH_2OH
>
> (iii) $H_2S_2O_8$
>
> (iv) $HClO_4$

(b) Define electronegativity. What are the different scales of electronegativity? Explain briefly.

(c) In contrast to diamond, graphite conducts electricity. Explain.

(d) Give reasons for the following:

   (i) $PbCl_4$ is a strong oxidizing agent in comparison to $PbCl_2$.

   (ii) In Ellingham diagram, the graphs for metal to metal oxide all slope upwards.

<div align="right">(4.5, 4.25, 4, 3 × 2)</div>

2. (a) Describe multicenter bonding using diborane as an example.

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

   (c) (i) Fluorine always exhibit an oxidation state of -1. while other halogens also show positive oxidation states. Give reason.

   (ii) Why solutions of alkali metals in liquid ammonia are conducting, paramagnetic and blue in color?

   (d) (i) Why PCl_5 is a Lewis acid and not a Lewis base while PCl_3 is both?

   (ii) Among alkali metals halides lattice energy for LiF is greatest and smallest for CsI. Discuss.

<div align="right">(4.75, 4, 2 × 2, 3 × 2)</div>

3. (a) Carbon can be used to reduce any metal oxide if a sufficiently high temperature is used. Justify this statement using Ellingham diagram.

   (b) Discuss the following statements.

   (i) $BeCl_2$ is the most covalent alkaline earth metal chloride.

   (ii) Nitrogen exists as diatomic molecule, N_2, whereas phosphorous exists as tetratomic molecule.

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

   (i) Mond's Process

   (ii) Allotropes of Sulphur

   (iii) Hydrometallurgy

<div align="right">(4.75, 3 × 2, 4 × 2)</div>

SECTION B

(PHYSICAL CHEMISTRY)

Attempt any **two** *questions in this section.*

Question No. 1 is compulsory

1. Attempt the following questions briefly:
   (a) What is the effect of temperature on viscosity of gases and liquids?   3
   (b) How many element of symmetry present in NaCl crystal, explain them?   3
   (c) Differentiate order and molecularity of a reaction.   3
   (d) Explain law of rational indices.   3.5
   (e) Calculate the activation energy of a reaction whose reaction rate at 27^0 C gets doubled for 10^0 C rise in temperature.   3.5
   (f) Derive Bragg's Equation.   3.5

2. (a) Derive integrated rate expression for second order reaction assuming concentration of reactants to be different.
   (b) The half-life period of a substance is 50 minutes at a certain concentration. When the concentration is reduced to one half of the initial concentration, the half-life period is 25 minutes. Calculate order of the reaction.
   (c) Calculate the miller indices for following crystal planes
           i.   2a,-3b,-3c
           ii. 6a, 3b,3c

                                                                                   (6,6,6)

3. (a) Calculate the interplanar spacing (d_{hkl}) for a cubic system between the set of planes 111 and 222. Assuming the edge length of the unit cell is a.
   (b) Explain various defects in crystals.
   (c) Write short notes on any two-
           (i)   Andrews Isotherms of CO_2,
           (ii)   Collision Frequency (Z11),
           (iii)   Viscosity of liquids and its determination.

                                                                                   (6,6,6)

,

Sr. No. of the Question Paper :
Unique Paper Code   : 42177926

Name of the paper   : Organometallics,Bio-Inorganic Chemistry,Polynuclear

                               Hydrocarbons and UV,IR Spectroscopy

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

Semester   : VI

Duration   : 2 Hours

 Maximum Marks   : 75

Instructions for Candidate

   [1] Attempt **two** questions each from Section A and Section B

   [2] All questions carry equal marks

Section A

1. a). What is meant by hapticity of a ligand? Give an example of ligands with hapticity
       3, 5 and 6.
    b).Hemoglobin becomes saturated with oxygen in the lungs and then deoxygenated in
       the capillaries ,discuss.

    c). Write down the method of preparation of Potassium permanganate from
        pyrolusite ore. Why is it intense purple in colour?

    d) How is iron transferred from storage sites to the sites for incorporation

        in haemoglobin?

    e) What is synergic effect? How does it account for the stability of carbonyls with

       transition metals in low oxidation states? Which one will have higher

       Fe – C bond order in $Fe(CO)_5$ & $[Fe(CO)_4]^{2-}$? Justify your answer.

                                                                    (1.75,3,4,4, 6)

2 . a) What do you mean by essential, trace and toxic elements in biological
          system. Give an example of essential trace metal ion in human beings.

    b) What is meant by π acidity? Why is CO a π acid ligand?

.

c) In solid phase, $Co_2(CO)_8$ shows IR CO stretching frequencies in two different regions, 2100-2000 cm^{-1} and 1880-1850 cm^{-1}. Explain with relevant structures the changes if any, occur when solid compound is dissolved in hexane .

d) What are peroxo compounds of chromium? Give the structures of any two .

e) How is the unequal concentration of Na^+ and K^+ ions in extra cellular and intracellular fluid controlled in the human body? Give a diagrammatic representation of the process and explain the mechanism involved in it.

What is the source of energy in it?

(1.75,3,4,4, 6)

3. a). State Effective atomic number rule. What are effective atomic numbers of the metal

atoms in;

(i)$V(CO)_6$ (ii)$[Fe(CO)_4]^{2-}$ (iii)$Co_2(CO)_8$

b). Discuss Bohr's effect.

c). Name the metal involved in following metallobiomolecules

(i)Transferrin   (ii)Chlorophyll   (iii)Myoglobin (iv) Vitamin B12
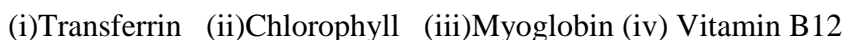
d) Write the chemical composition of
(i) blue violet peroxochromium(VI) species.
(ii) Prussian blue
(iii) Sodium Nitroprusside
(iv) Sodium Cobaltinirite
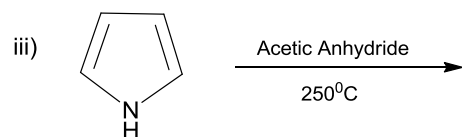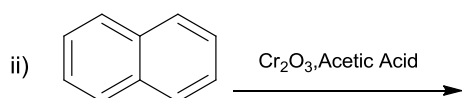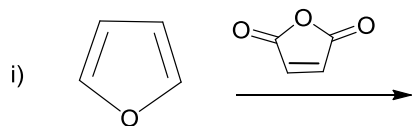
e) Write down any one method of preparation of a metal carbonyl. Give suitable example. Draw the structures of

(i) Methyl lithium (ii) Zeise's salt
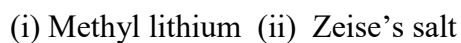
(1.75,3,4,4, 6)

Section B

1 a) Complete the reactions:

i)

ii) Cr_2O_3, Acetic Acid

iii) Acetic Anhydride, 250^0C

IV) CH_2N_2

V) $Na_2Cr_2O_7, H_2SO_4$

vi) SO_3, Pyridine

vii) HCHO / HCl

viii) Raney Ni

ix) HCN, HCl / H_2O

x) KMnO4
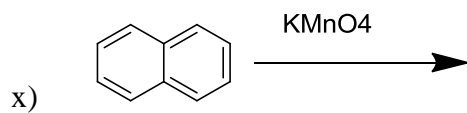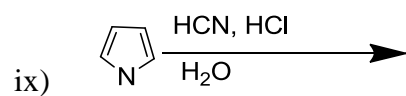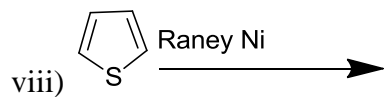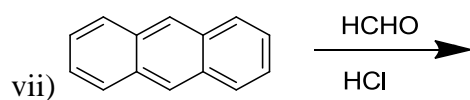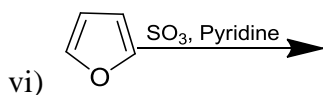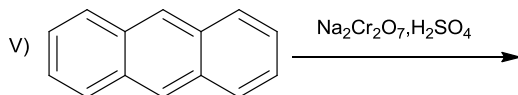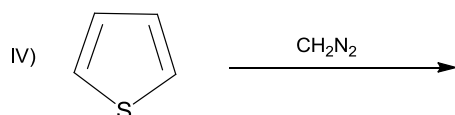
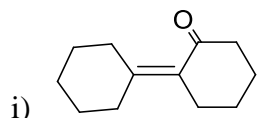b) Sulphonation of naphthalene yields different products at low and high temperatures. Explain.

c) Furan acts as a good conjugated diene in Diel's Alder reaction but pyrrole and thiophene do not. Explain

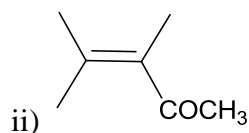d) Pyridine is stronger base than pyrrole but weaker than aliphatic amines.

e) Fill in the blank: Number of resonating structures in naphthalene are _____
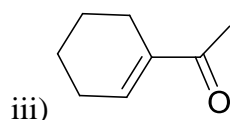
(10, 3, 2,3, 0.75)
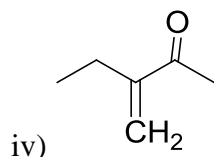
2 a) Calculate the λmax for the following compounds:

i)

Base Value of λmax = 221nm

ii) COCH$_3$

Base Value of λmax = 237nm

iii) O

Base Value of λmax = 249nm

iv) CH$_2$

Base Value of λmax = 258nm

b) How will you distinguish between CH_3CH_2-CHO and CH_3-CO-CH_3 using IR spectrum.

c) Explain the synthesis of ethylacetoacetate by Claisen ester condensation with mechanism.

d) Electrophillic substitution reaction in 5 membered aromatic heterocyclic compounds are preferably favoured at 2-position and not at 3-position.

e) Fill in the blank: Number of modes of vibration in CO_2 molecule is _____.

(12, 2, 4, 2, 0.75)

3 a) Give the synthesis of following compounds from ethyl acetoacetate: (any three)

i) 3-butyl-2-hexanone

ii) Succinic acid

iii) 3-ethyl pentane-2-one

iv) 3-butyl-2-hexanone

b) Isolated double bonds absorbs at lower wavelength as compared to conjugated double bond. Justify the statement.

c) The C_2-C_3 bond of naphthalene has lesser double bond character than C_1-C_2. Explain

d) Arrange $C_6H_5NH_2$, $(C_6H_5)_2NH$, NH_3, CH_3NH_2, $(C_6H_5)_3N$ in decreasing order of their basic strength.

e) Fill in the blank: Dipole moment of pyrrole is _____ as that of corresponding tetrahydropyrrole.

(9, 3, 3, 3,0.75)