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

Sr. No. of Question Paper : 2997

Unique Paper Code : 32171402

Name of the Paper : Organic Chemistry III : Heterocyclic Chemistry

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

Semester : IV

Duration : 3 Hours   Maximum Marks : 75

Instructions for Candidates

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

2. Attempt **six** questions in all.

3. Question No. **1** is compulsory and carries **15** marks.

4. All other questions are of **12** marks each.

1. (a) An organic compound A (C_3H_7NO) on treatment with bromine and aqueous NaOH forms a compound B (C_2H_7N). B on treatment with $NaNO_2$ and dil. HCl gives C (C_2H_6O) along with the

evolution of N_2 gas. C forms iodoform with iodine and aqueous Na_2CO_3. Identify 'A', 'B' and 'C'. Give the sequence of the reactions involved. Name the reaction involved in the conversion of A to B with mechanism.

(b) Sulphonation of Naphthalene gives different products at low and high temperatures. Give reactions and explain.

(c) Explain the order of reactivity of furan, thiophene, and pyrrole towards electrophilic substitution reaction. Draw suitable structures to justify your answer.

(d) Citral forms two semicarbazones with different melting points. Justify your answer with structures and their names.   (6,3,3,3)

2. (a) Describe Haworth's method for the synthesis of Phenanthrene.

(b) Electrophilic substitution reaction in Anthracene occurs preferably at C-9. Explain by drawing the relevant resonating structures.

(c) C_1-C_2 bond in Naphthalene is shorter than C_2-C_3 bond. Explain.

(d) Write the sequence of reactions which establish that naphthalene consists of two benzene rings fused together. (3,3,3,3)

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

(b) Arrange the following compounds in order of decreasing basic strength. Give reason to justify your answer :

Cyclohexylamine; Aniline; p-Toluidine

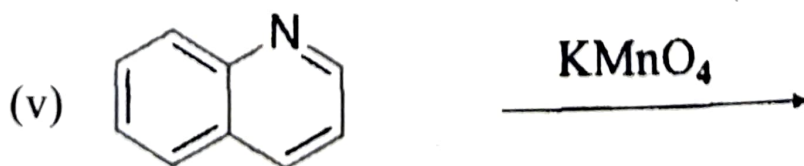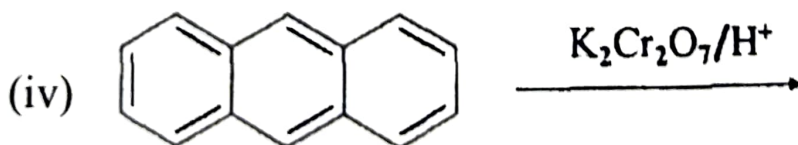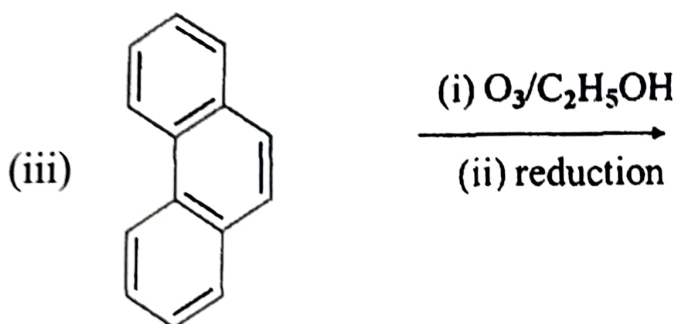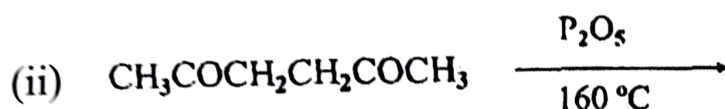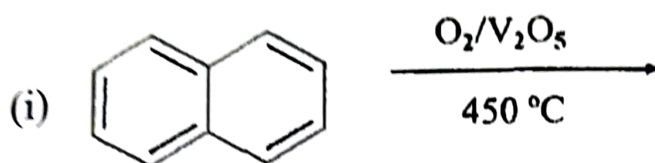(c) How will you distinguish between nitriles and isonitriles? Give relevant reactions.

(d) Write the mechanism of base catalysed hydrolysis of alkyl nitriles. (3,3,3,3)
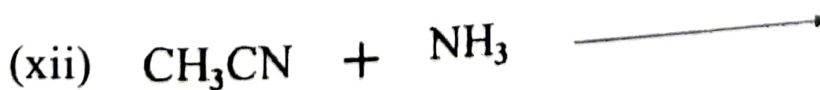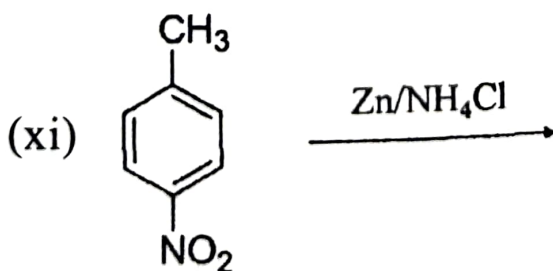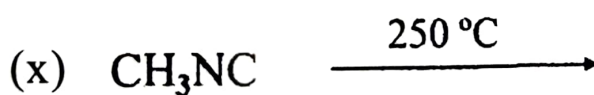
4. (a) Carry out the following conversions (any three) :

(i) Naphthalene into β-naphthol

(ii) Thiophene into thiophene-2-carboxylic acid

(iii) Aniline into p-bromoaniline

(iv) Nitrobenzene into m-bromophenol

(b) Coupling reactions of diazonium salts take place in either mild acidic or mild alkaline conditions. Explain using suitable reactions. (3,3,3,3)

5. Write the products formed : **(any 12)**

(i) $\xrightarrow[450\,°C]{O_2/V_2O_5}$

(ii) $CH_3COCH_2CH_2COCH_3$ $\xrightarrow[160\,°C]{P_2O_5}$

(iii) $\xrightarrow[\text{(ii) reduction}]{\text{(i) } O_3/C_2H_5OH}$

(iv) $\xrightarrow{K_2Cr_2O_7/H^+}$

(v) $\xrightarrow{KMnO_4}$

(vi)

$$\text{pyridine} \xrightarrow[100\ ^{\circ}\text{C}]{\text{n-}C_4H_9Li}$$

(vii)

$$\text{indole} \xrightarrow[120\ ^{\circ}\text{C}]{SO_3/\text{pyridine}}$$

(viii)

$$\text{furyl-CHO} \xrightarrow[NaOC_2H_5]{CH_3CH_2COOC_2H_5}$$

(ix)

$$\text{thiophene} \xrightarrow[180\ ^{\circ}\text{C}]{H_2/\text{Raney Ni}}$$

(x) $CH_3NC \xrightarrow{250\ ^{\circ}\text{C}}$

(xi)

$$\text{p-nitrotoluene} \xrightarrow{Zn/NH_4Cl}$$

(xii) $CH_3CN + NH_3 \longrightarrow$

(xiii) + $\xrightarrow[\Delta]{\text{xylene}}$

(xiv) + $\xrightarrow{\text{dil NaOH}}$ (12×1=12)
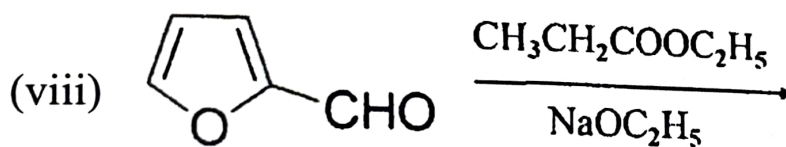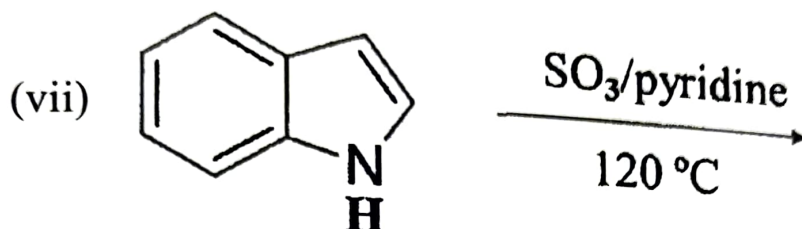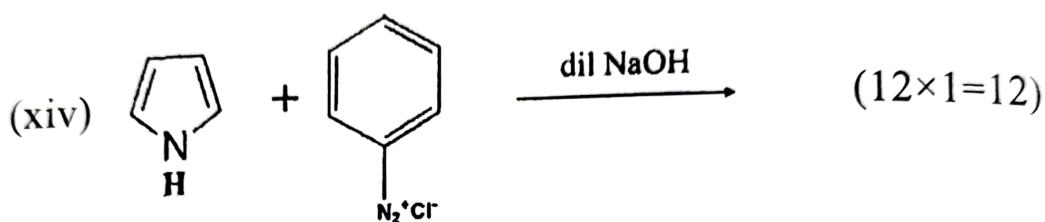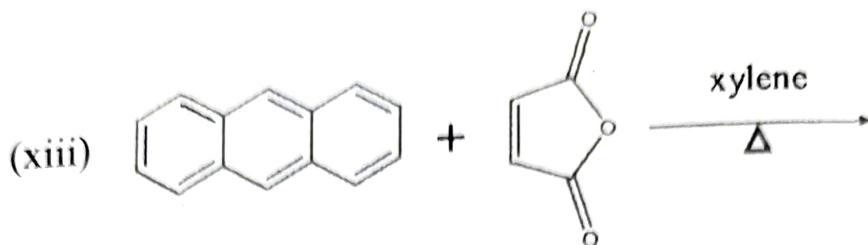
6. (a) Define 'Isoprene rule'. Mark out the isoprene units in the following compounds with dotted lines.
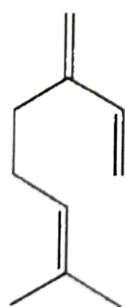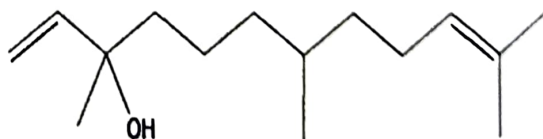

(i)

(ii)

(b) How the positions of two double bonds in citral is established? Give the relevant reactions.

(c) Give synthesis of nicotine from nicotinonitrile.

(d) Explain the reaction which indicates the position of linkage between pyridine and N-methyl pyrrolidine in nicotine.

(3,3,3,3)

7. (a) Explain the fact that pyridine reacts with electrophiles as well as nucleophiles with the help of resonating structures.

(b) Electrophilic substitution reaction in Indole occurs at C-3. Explain by drawing suitable resonating structures.

(c) Pyrrole undergoes ring expansion with $CHCl_3$ and NaOH. Give the reaction and its mechanism.

(d) The reactions of furan cannot be done in the acidic medium. Give reason and the reaction involved.

(3,3,3,3)

8. (a) Write short notes on the followings (any two) :

(i) Skraup synthesis of quinoline

(ii) Hantzsch-pyridine synthesis

(iii) Hinsberg method

(b) Outline the reaction sequence involved in the Hoffmann exhaustive methylation procedure of hydrogenated pyridine. (4,4,

[This question paper contains 12 printed pages.]   04/6/24
05/6/24

Your Roll No. ....

Sr. No. of Question Paper : 3108

Unique Paper Code   : 32171403

Name of the Paper   : Physical Chemistry Conductance & Chemical Kinetics

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

Semester   : IV

Duration : 3 Hours   Maximum Marks : 75

Instructions for Candidates

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

2. Attempt **six** questions in all.

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

4. Attempt at least **one** question from each Section.

5. Use of scientific calculators is permitted.

NOTE:

$R = 8.314$ $JK^{-1}mol^{-1}$, $h = 6.626 \times 10^{-34}$ Js, $k_B = 1.381 \times 10^{-23}$ JK^{-1}, $F = 96485$ C mol^{-1}

P.T.O.

3

1. Explain any **five** of the following :

   (a) Quantum efficiency of Fluorescence decreases with the increase in concentration of the solution.

   (b) Role of Uranyl ion in photochemical decomposition of oxalic acid.

   (c) The first order reaction never achieves completion.

   (d) The activation energy of a reaction cannot be zero or negative.

   (e) The molar conductivity of Li^+ ion is less than that of Cs^+ ion in aqueous medium.

   (f) The transport number of Cd^{2+} in concentrated solution of CdI_2 is negative.   (5×3)

SECTION A

2. (a) Compare the rate constants as given by Collision Theory and the Activated Complex Theory. Hence, the steric factor p of collision theory may be interpreted in terms of entropy of activation.
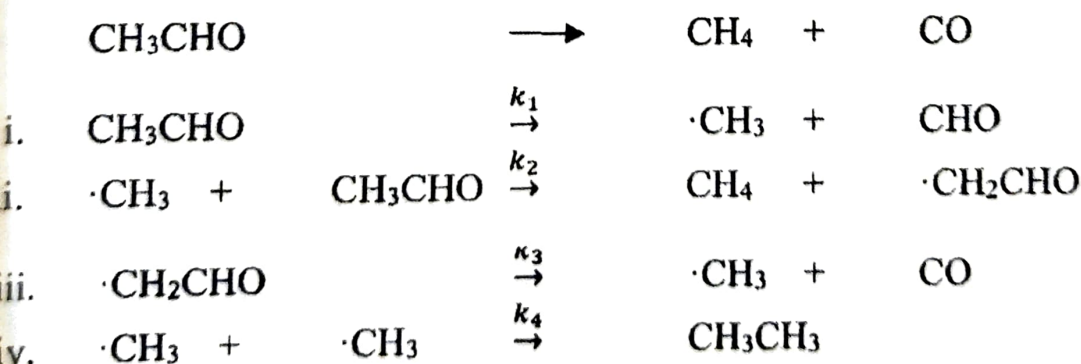   (5)

(b) The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

is first order and has a rate constant 2.24×10^{-5} s^{-1} at 320°C. What fraction of a sample of $SO_2Cl_2(g)$ remains after being heated for 5 Hrs. at 320°C? How long will a sample of SO_2Cl_2 (g) take to decompose 92.0% of the initial amount present at 320°C?   (4)

(c) Derive an expression for half-life time of a nth order reaction.   (3)

3. (a) Considering the following mechanism for the thermal decomposition of acetaldehyde :

$CH_3CHO \longrightarrow CH_4 + CO$

i. $CH_3CHO \xrightarrow{k_1} \cdot CH_3 + CHO$

ii. $\cdot CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + \cdot CH_2CHO$

iii. $\cdot CH_2CHO \xrightarrow{k_3} \cdot CH_3 + CO$

iv. $\cdot CH_3 + \cdot CH_3 \xrightarrow{k_4} CH_3CH_3$

Derive the differential rate law for the formation of CH_4 using steady state approximation and also determine the chain length for the same reaction.
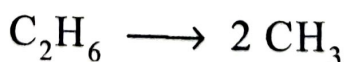
(4)

(b) For a reversible first-order reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$
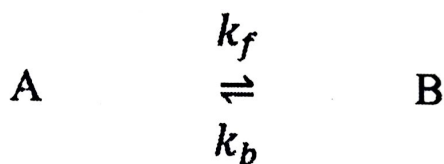
$k_f = 10^{-2}$ s^{-1} and $\dfrac{[B]eq}{[A]eq} = 4$. If $[A]_0 = 0.01$ mol

L^{-1} and $[B]_0 = 0$, what will be concentration of B after 30 s?

(4)

(c) The rate constant for the dissociation of ethane

$$C_2H_6 \longrightarrow 2\,CH_3$$

is given by $k = 5 \times 10^6 \exp\left(\dfrac{-368\ kJ}{RT}\right)$.

Calculate the entropy of activation for this reaction at 850 K.

(4)

4. (a) The initial rate of oxidation of sodium succinate to form sodium fumerate in presence of the enzyme succinate dehydrogenase at different sodium succinate concentrations is given below

Sodium succinate conc $\times 10^3$/mol dm^{-3}	10.0	2.0	1.0	0.5	0.33
Initial rate $\times 10^6$ mol s^{-1}	1.17	0.99	0.79	0.62	0.50

Determine the Michaelis constant and the limiting rate of equation. (5)

(b) Given below is the mechanism of acid-base catalysis

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$$

$$SH^+ + H_2O \overset{k_2}{\rightarrow} P + H_3O^+$$
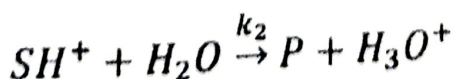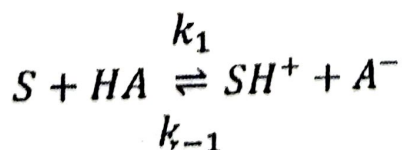
Derive the expression for the rate of formation of product.

$$\frac{dP}{dT} = \frac{k_2 k_1 [S][HA]}{k_{-1}[A^-] + k_2}$$

Show under what conditions a given catalytic reaction may be classified into general acid catalysis and a specific hydrogen ion catalysis.

(4)

(c) Define Turnover number of enzymes. (3)

SECTION B

5. (a) (i) The amide ion in liquid ammonia has an abnormally high transference number. Explain.

(ii) In the conductometric titration, the solution to be added from the burette is much stronger than the solution taken in the conductometric cell. Why? (2+2)

(b) Discuss Hittorf's method to determine the transference number of ions. (4)

(c) The specific conductance of a saturated solution of BaSO, is 3.48×10^{-4} S/m. The conductivity of pure water is 0.50×10^{-4} S/m. Calculate the solubility and solubility product of $BaSO_4$ (Limiting ionic conductance of Ba^{2+} and SO_4^{2-} are 127.26×10^{-4} and 160.04×10^{-4} Sm^2mol^{-1} respectively). (4)

6. (a) At 25°C, the specific conductance of distilled water is 58.0×10^{-7} Sm^{-1} and the λ°_m values of H^+ and OH^- ions are 349.8×10^{-4} and 198.5×10^{-4} Sn^2mol^{-1}, respectively. Assuming that λ_m differs very little from λ°_m, calculate the ionic product of water at 25°C. (4)

(b) What is Transference number? How the

transference number is related to the absolute velocity of the ion. Derive the related expression.

(4)

(c) A solution of 0.10 M in LiCl with conductivity 1.06×10^{-2} S/cm is placed in a moving boundary cell of cross-sectional area 1.17 cm². It was electrolyzed for 131 minutes with a constant current of 9.42 milliamperes. The Li^+ was observed to move a distance of 2.08 cm. What is the transport number of Li^+ in the solution? (4)

7. (a) (i) State Faraday's Laws of Electrolysis.

(ii) How does ionic mobility differ from ionic speed? What is the unit of ionic mobility?

(2+2)

(b) State Kohlrausch Law of independent migration of Ions. How will you calculate the molar

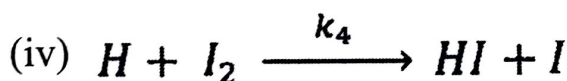conductance and equivalent conductance at infinite dilution of Potash alum $[K_2SO_4.Al_2(SO_4)_3.24H_2O]$? How are they related to each other?   (4)
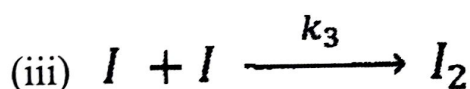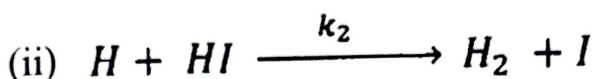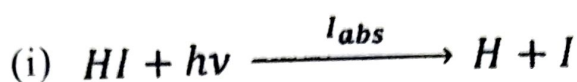
(c) At 25°C a solution of KCl having a conductivity of 0.14088 S/m exhibits a resistance of 654 ohm in a particular conductivity cell. In this same cell, a 0.10 mol/L solution of NH_4OH has a resistance of 2524 ohm. Calculate

  (i) the cell constant

  (ii) the molar conductivity of NH_4OH solution

  (iii) the degree of dissociation of the 0.10 mol/L NH_4OH

  (iv) the dissociation constant of NH_4OH.

(Limiting molar ionic conductivities of NH_4^+ and OH^- are 73.55×10^{-4} and 198.3×10^{-4} Sm^2 mol^{-1} respectively)   (4)

SECTION C

8. (a) Given the following mechanism

(i) $HI + h\nu \xrightarrow{I_{abs}} H + I$

(ii) $H + HI \xrightarrow{k_2} H_2 + I$

(iii) $I + I \xrightarrow{k_3} I_2$

(iv) $H + I_2 \xrightarrow{k_4} HI + I$

Show that the quantum efficiency of the decomposition of HI is

$$\varphi_y = \frac{2}{1 + \dfrac{k_4 [I_2]}{k_2 [HI]}}$$

(5)

(b) A mixture of hydrogen and chlorine was irradiated with radiation of wavelength 400 nm. In a given

interval of time, 7×10^{-5} J were absorbed by the reactant chlorine. If φ_{HCl} is 2.6×10^6 J, how many moles of HCl are formed per joule of energy absorbed. (4)

(c) The quantum yield for the photochemical reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$
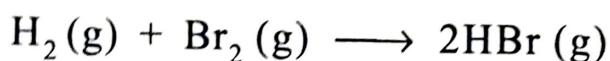
Is ~ 0.01 while that for the reaction.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
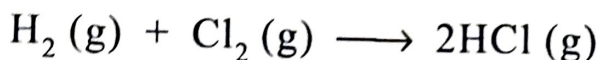
is $\sim 10^4 - 10^6$. Explain. (3)

9. (a) A monochromatic light of certain wavelength was passed through a solution of certain concentration using a cell of 0.5 m and 25% of the incident light was absorbed. What is its absorbance? If the concentration of the solution is doubled, what will be the length of the cell which absorbs 60% of the incident light. (4)

(b) Discuss the asymmetric effect and electrophoretic

effect. How these effects can be minimized?

(4)

(c) Write short notes on any **one** of the following :

(i) Pseudo-unimolecular reactions

(ii) Chemical Actinometer (4)

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

Sr. No. of Question Paper : 4132

Unique Paper Code : 2172012403

Name of the Paper : Electrochemical Cells and Chemical Kinetics
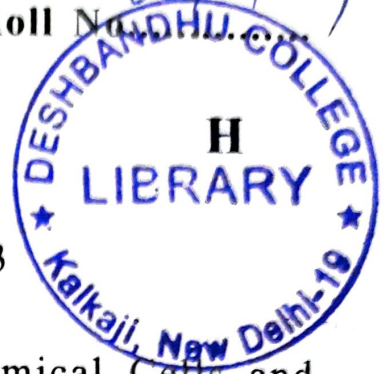
Name of the Course : **B.Sc. (H) Chemistry**

Semester : IV

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. **First** question is Compulsory.

3. Use of a Scientific calculator is permitted.

4. Graph paper will be provided.

P.T.O.

1.   (Attempt any **Five** Parts)

(a) First-order reaction never goes to completion. Explain.

(b) It is rare for a reaction to have a molecularity of more than three.

(c) A first order reaction, A → products, has a rate of reaction of 0.00250 M s^{-1} when [A] = 0.484 M.
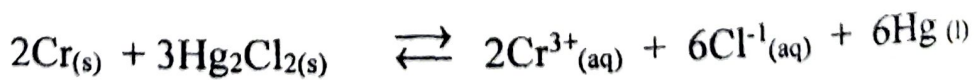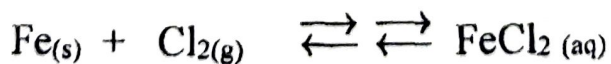
   (i) What is the rate constant, k, for this reaction?

   (ii) Does $t_{3/4}$ depend on the initial concentration?

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

(e) Why can we not use a voltmeter for determining the e.m.f. of a galvanic cell?

(f) Set up the galvanic cell for the following reactions:

$$Fe_{(s)} + Cl_{2(g)} \rightleftarrows \rightleftarrows FeCl_{2\,(aq)}$$

$$2Cr_{(s)} + 3Hg_2Cl_{2(s)} \rightleftarrows 2Cr^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 6Hg_{(l)}$$

(g) What is the difference between the Turnover Number (k_{cat}) and the Michaelis constant (K_M)? (5×3)

2. (a) Describe briefly the potentiometric method for the determination of emf of a cell.

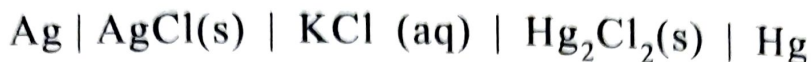(b) Determine the cell reaction and EMF for the cell at 25°C

$$Mg(s) \mid MgI_2(0.1 \text{ M}) \mid I_2(s) \mid Pt(s)$$
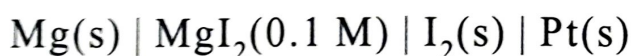
Given that : $E^\circ_{I^-|I2} = 0.535$ V and $E^\circ_{Mg^{2+}|Mg} = -2.363$ V

(c) Describe the calomel half cell and derive its Nemst equation. (3×5)

3. (a) Determine the cell reaction and E_{cell} for the given cell at 25°C. Assume activity and fugacity equal to molar concentration and pressure (atm), respectively

$$Ag \mid AgBr(s) \mid HBr \ (0.02 \text{ mol dm}^{-3}) \mid H_2(0.5 \text{ bar}) \mid Pt$$
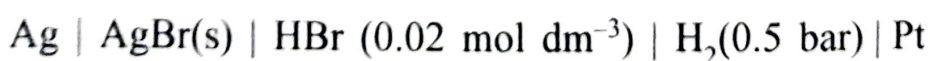
$$E^\circ_{Br^-} \mid AgBr \mid Ag = 0.0713 \text{ V}$$

(b) The emf of the cell

$$Ag \,|\, AgCl(s) \,|\, KCl \,(aq) \,|\, Hg_2Cl_2(s) \,|\, Hg$$

is 0.0455V at 298 K and the temperature coefficient is 3.38×10^{-4} VK^{-1}. What is the reaction taking place in the cell and what are the free energy, enthalpy and entropy changes at 298 K?

(c) Describe the glass electrode. Explain, how the pH of a solution is determined using the glass electrode. Also mention its limitations. (3×5)

4. (a) Derive the expression for calculating liquid junction potential for a cell in which electrode are reversible with respect to anion. How can it be eliminated?

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

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

Given, $E°_{Fe3+,\ Fe^{2+}} \,|\, Pt = 0.771$ V and $E°_{Sn^{4+},\ Sn^{2+}} \,|\, Pt = 0.150V$

(c) What is the principle of potentiometric titration? Briefly discuss the potentiometric titration curve for acid-base titration. (3×5)

5. (a) What is the difference between order and molecularity of the reaction?

(b) Derive the integrated rate equation for the zero-order reaction. How the value of rate constant can be determined using the graphical method?

(c) In the reduction of nitric oxide 50% of the reaction was completed in 140 seconds when the initial pressure was 258 mmHg and in 224 seconds when the initial pressure was 202 mmHg. Find the order of the reaction. (3×5)

6. (a) Describe the collision theory of bimolecular gaseous reactions Show that it leads to the rate expression

$$r = p\{\pi \, \sigma^2_{AB}(\{\frac{8KT}{\pi\mu}\}^{1/2} \, N_A{}^* \, N_B{}^* \,) \exp^{(-E_o} RT)$$

(b) Discuss the effect of temperature on reaction rates. How is the activation energy of a reaction calculated?

(c) Lindemann mechanism for the first order reaction is as follows :

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A \qquad \text{(in rapid equilibrium)}$$

$$A^* \overset{k_2}{\longrightarrow} product \qquad \text{(slow)}$$

Show that it leads to

$$\frac{d(product)}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$$

Under what conditions will the order of the reaction be equal to one? (3×5)
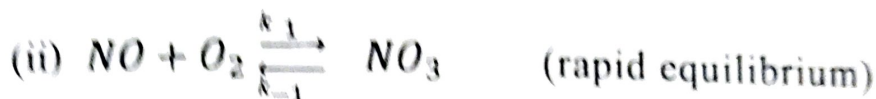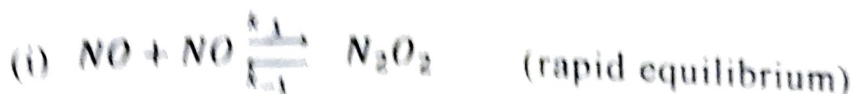
7. (a) For the reaction

$$C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$$

The rate constant was found to have a value of 5.03×10^{-2} mol^{-1} dm^3 s^{-1} at 289 K and 6,71 mol^{-1} dm^3 s^{-1} at 333K. What is the activation energy of reaction. What is the rate constant at 305K.

(b) For the reaction :

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2$$
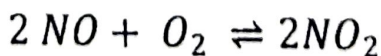
Two mechanisms have been proposed:

(i) $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (rapid equilibrium)

$N_2O_2 + O_2 \overset{k_2}{\rightarrow} 2NO_2$ (slow)

(ii) $NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3$ (rapid equilibrium)

$NO + NO_3 \overset{k_2}{\rightarrow} 2NO_2$ (slow)
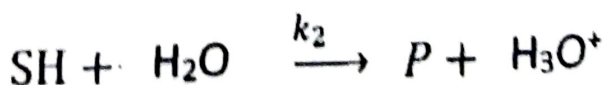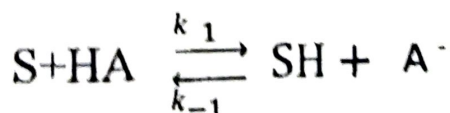
Show that both the mechanisms lead to the same rate law.

(c) Write short note :

    (i) Chain Reactions

    (ii) Steady State Approximation   (3×5)

8.   (a) The mechanism of an acid-base-catalyzed reaction is given below. Derive the corresponding rate law

$$S+HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH + A^-$$

$$SH + H_2O \overset{k_2}{\longrightarrow} P + H_3O^+$$

$$\frac{d(P)}{dt} = \frac{k_2 k_1 [S][HA]}{k_{-1}[A-] + k_2}$$

Under what conditions a given catalytic reaction may be classified into a general acid catalysis and specific hydrogen ion catalysis?

(b) (i) Differentiate between Homogeneous and heterogeneous catalysis.

(ii) The use of a catalyst provides an alternate path. Comment.

(c) Discuss briefly the kinetics of Heterogeneous catalysis for unimolecular surface reactions.

(3×5)

[This question paper contains 3 printed pages.]
Sr. No. of Question Paper: 4183
Unique Paper Code: 2173012011
Name of the Paper: DSE: Reactions, Reagents and Chemical Process
Name of the Course: B.Sc. (Hons) Chemistry
Semester: IV
Duration: 3 hours
Maximum Marks: 90

Your Roll No. ....

10/6/2034

Instructions for candidates:

1. Write your Roll. No. on the top immediately on receipt of this question paper.
2. Attempt any six questions. All parts of a question should be attempted together.
3. Each question carries 15 marks.

1. Explain the following reaction with suitable mechanism.
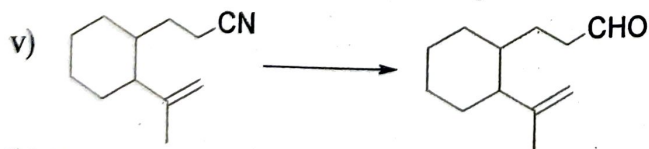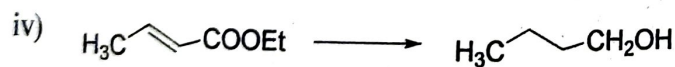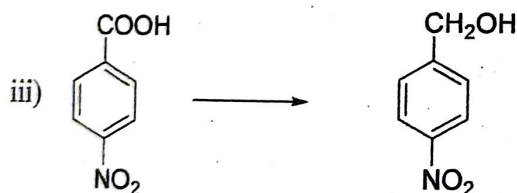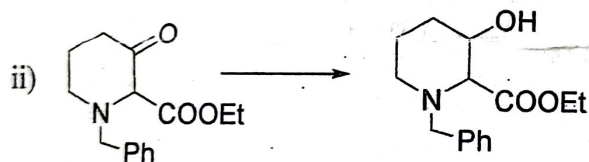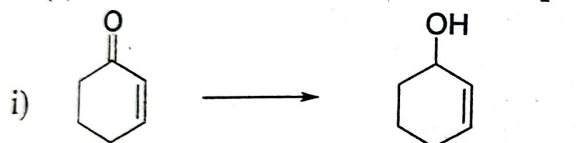   (a) Bischler-Napieralski Reaction   (5, 5, 5)
   (b) Darzens reaction
   (c) Demjanov rearrangement

2. (a) The most suitable reagents for performing the following transformation are?   (1x5, 2x5)

i)

ii)

iii)

iv) H₃C—CH=CH—COOEt ⟶ H₃C—CH₂—CH₂—CH₂OH

v)

(b) Write the structure of following reagents
   (i) Tebbe's reagent
   (ii) TPAP reagent
   (iii) ABNO reagent
   (iv) PMHS reagent
   (v) DEAP reagent

3 (a) What is synthetic utility of DAIBAL-H and LAH in organic synthesis explain with suitable example.   (10, 5)

   (b) Write the structure and synthetic application of following reagents
   (i) Swern Reagent
   (ii) Jones Reagent

4. (a) What is Wacker oxidation. Explain role of catalyst and co-catalyst used in Wacker oxidation with suitable example. (5, 5, 5)
   (b) Which reagent/ catalyst used in the following reactions
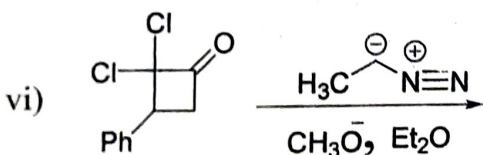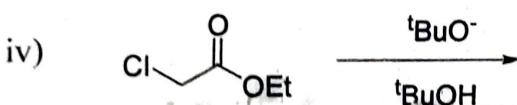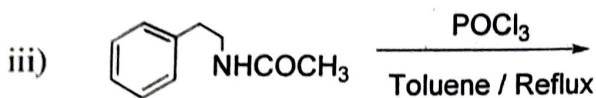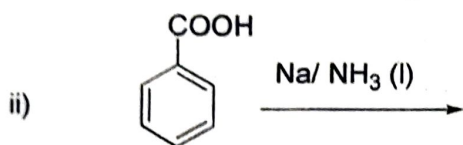   (i) Wittig reaction
     (ii) Corey Kim Oxidation reaction
     (iii) Prevost Reaction
  (c) Explain the Heck reaction with suitable mechanism.

5. (a). Complete the following reaction by giving major product. (12, 3)

i)
C_6H_5O — ≡ $\xrightarrow[\Delta]{C_6H_5CH_2N_3}$

ii)
COOH
(benzene ring) $\xrightarrow{Na/ NH_3 (l)}$

iii)
(benzene ring)–CH$_2$–NHCOCH$_3$ $\xrightarrow[\text{Toluene / Reflux}]{POCl_3}$

iv)
Cl—CH$_2$—C(=O)—OEt $\xrightarrow[^tBuOH]{^tBuO^-}$

v)
(epoxide)—COOEt $\xrightarrow[\text{2. HCl}]{\text{1. NaOH}}$

vi)
(cyclobutanone with Cl, Cl, Ph substituents) $\xrightarrow[CH_3\bar{O}, Et_2O]{H_3C-\overset{\ominus}{\underset{}{}}\overset{\oplus}{N}\equiv N}$

  (b) What is Birch reduction? Explain with suitable example.

6. (a) What is Suzuki coupling reaction? Write the steps involves in the mechanism of involves in Suzuki coupling reaction. (5, 5, 5)
  (b) Write the reaction and mechanism of Julia olefination reaction?
  (c) Which reactant and reagent is used in Chugaev Reaction.
7. (a) Explain large scale process with at least two suitable examples? (5, 5, 5)
  (b) Explain validation of large-scale process with suitable examples?
  (c) Explain the stages of scale up process with suitable examples?
8. Write short notes on following (5, 5, 5)
  (a) Halogenation & types of halogenations
  (b) Swern Oxidation.
  (c) Fenton's reagent.