**Sr. No. of Question Paper :** 1142

A

Unique Paper Code : 32171401

Name of the Paper : Inorganic Chemistry – III

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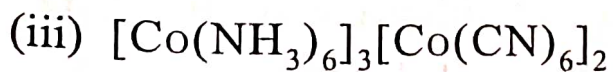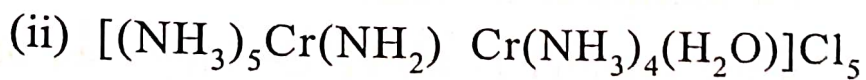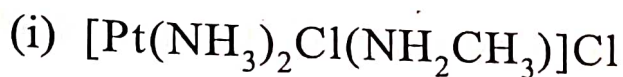
Semester : IV

Duration : 3.5 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. **All** questions carry equal marks.

1. (a) Name of the following complexes according to the IUPAC system of nomenclature :

   (i) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

   (ii) $[(NH_3)_5Cr(NH_2) Cr(NH_3)_4(H_2O)]Cl_5$
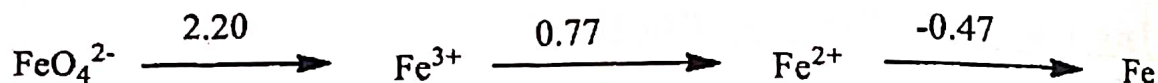
   (iii) $[Co(NH_3)_6]_3[Co(CN)_6]_2$

P.T.O.

(b) Write the formulae of the following complexes :

(i) Sodium bis(thiosulphato)argentate(I)

(ii) Triamminechlorocyanonitrocobalt(III)

(iii) Potassium diaquatetrabromovanadate(III)

(c) Given below is the Latimer diagram for Fe in acidic medium :

$$FeO_4^{2-} \xrightarrow{2.20} Fe^{3+} \xrightarrow{0.77} Fe^{2+} \xrightarrow{-0.47} Fe$$

(i) Why $FeO_4^{2-}$ is strong oxidising agent?

(ii) Is there any tendency of $Fe^{2+}$ to reduce to Fe. Give reasons.

(d) A strong oxidizing agent(A) on heating with KCl and conc. $H_2SO_4$ gives red coloured gas B which on passing through potassium hydroxide solution gives yellow solution C. C may also be obtained on heating A on treatment with conc. $H_2SO_4$ gives a red product D which decomposes on heating to give a product. Identify A, B, C, D.

(3,3,3,3.5)

2.  (a) Which of the following is more stable :

$[Co(en)_3]^{3+}$,    $[Co(dien)_3]^{3+}$
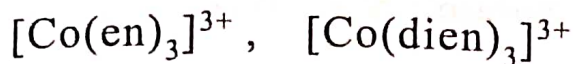
(b) Justify the presence of copper in the transition series.

(c) Explain $d_\pi - p_\pi$ bonding in complexes.

(d) Explain Jahn Teller effect.

Which of the following complex have all equal bond length and why?

$[CrF_6]^{3-}$ and $[MnF_6]^{3-}$                    (3,3,3,3.5)

3.  (a) Identify A, B, C, D in the following reactions :

(i) $[PtCl_4]^{2-}$ $\xrightarrow{NH_3}$ [A] $\xrightarrow{NH_3}$ [B]

(ii) $[Pt(NH_3)_4]^{2+}$ $\xrightarrow{Cl^-}$ [C] $\xrightarrow{Cl^-}$ [D]

(b) What happens when

(i) KI is added to $KMnO_4$ in acidic medium.

(ii) $SO_2$ is passed through acidified $K_2Cr_2O_7$ solution.

P.T.O.

(c) +3 is the most common oxidation state of lanthanides. Explain.

(d) $Fe_3O_4$ is inverse spinel while $Mn_3O_4$ is normal spinel. Explain on the basis of CFT.

(3,3,3,3.5)

4. (a) The pairing energy (P) for the $[Cr(H_2O)_6]^{2+}$ ion is 23000 cm$^{-1}$ and crystal field splitting ($\Delta_0$) is 14000 cm$^{-1}$. Calculate the crystal field stabilization energy in high spin and low spin state. Which state is more stable?

(b) 4d and 5d elements usually form low spin complexes. Justify.

(c) Tetrahedral complexes are high spin. Explain

(d) Using the valence bond theory method, work out following for $[Cr(CN)_6]^{3-}$

(i) Assign the electronic configuration to the central metal ion,

(ii) predict the type of hybridization involved,

(iii) geometry, and

(iv) the magnetic moment                    (3,3,3,3.5)

5.   (a) What are differences between valence bond theory and crystal field theory?

   (b) Explain Spectrochemical series.

   (c) Higher Oxidation states of transition elements are stabilized by small anions like $F^-$, $O^{2-}$. Explain.

   (d) For $Cr^{2+}$ octahedral complexes in strong and weak field, determine the (i) configuration in terms of $t_{2g}^x e_g^y$, (ii) number of unpaired electrons, and (iii) crystal field stabilization energy.          (3,3,3,3.5)

6.   (a) Write three differences between the characteristic features of lanthanides and actinides.

   (b) $Ce^{4+}$ ion is coloured whereas $Ce^{3+}$ ion is colourless. Why?

   (c) Work out the number of unpaired electrons in the following ions :

$$Eu^{2+}, \ Tb^{4+}, \ Lu^{3+}$$

   (Atomic number of Eu = 63, Tb = 65, Lu = 71)

   (d) What is lanthanide contraction? What are the major consequences of lanthanide contraction on the chemistry of d block elements?          (3,3,3,3.5)

P.T.O.

7. (a) The compound $CoCl_3.4NH_3$ gives one $Cl^-$ ion on the addition of $Ag^+$ ion. Draw the structure of the compound on the basis of Werner's coordination theory.

(b) Explain the following with suitable examples :

(i) Ionisation isomerism

(ii) Linkage isomerism

(c) Using valence bond theory, discuss hybridization and structure of the following :

(i) $[Cr(NH_3)_6]^{3+}$

(ii) $Ni(CO)_4$

(d) $[Fe(CN)_6]^{4-}$ ion is diamagnetic but $[Fe(CN)_6]^{3-}$ ion is paramagnetic in nature. Explain using V.B.T.

(3,3,3,3.5)

8. (a) Explain why does colour of $KMnO_4$ disappear when oxalic acid is added to its solution in acidic medium.

(b) $K_2Cr_2O_7$ is a good oxidising agent in acidic medium.

Explain.

(c) Write down the number of 3d electrons in each of the following ions :

    (i) $Cr^{3+}$

    (ii) $Fe^{3+}$

    (iii) $Cu^{2+}$

(d) Transition elements and their compounds are generally found to be good catalyst in chemical reaction. Discuss.       (3,3,3,3.5)

9. (a) Give the reasons for the following **(any two)** :

    (i) Mn(II) ion shows maximum magnetic character among the bivalent ions of first transition series.

    (ii) Cu(I) is diamagnetic while Cu(II) is paramagnetic.

    (iii) $Zn^{2+}$ salts are white while $Cu^{2+}$ salts are blue.

(b) Although $Cr^{3+}$ and $Co^{2+}$ ions have same number of unpaired electrons but the magnetic moment of

$Cr^{3+}$ is 3.87 B.M. and that of $Co^{2+}$ is 4.87 B.M. Explain.

(c) Explain why Fe(II) and Fe(III) form complexes with $CN^-$ ions but not with $NH_3$. (6,3,3.5)

[This question paper contains 8 printed pages.]

(13)   Your Roll No. 2.0.2.2

**Sr. No. of Question Paper :** 1369        A

Unique Paper Code        : 32171402

Name of the Paper        : Organic  Chemistry – III, Heterocyclic Chemistry

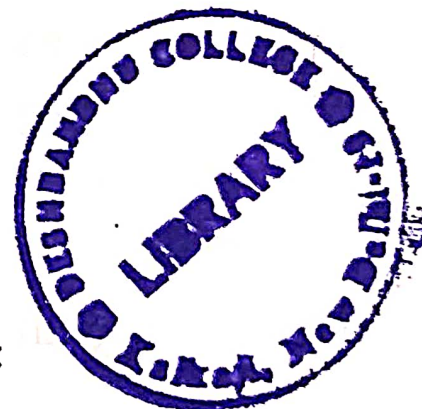Name of the Course        : **B.Sc. (Hons.) Chemistry**
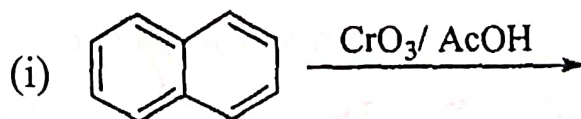
Semester        : IV

Duration : 3 Hours 30 Mins        Maximum Marks : 75
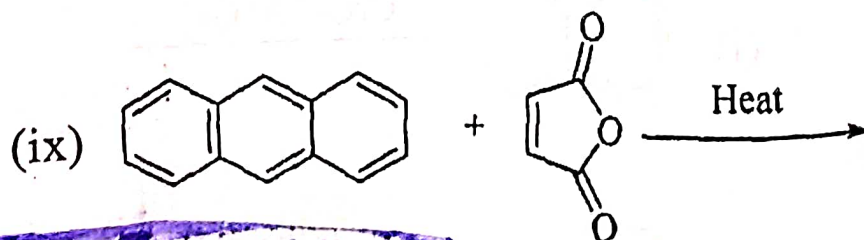
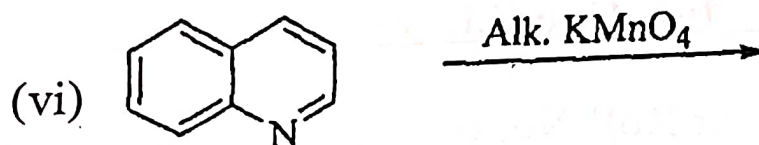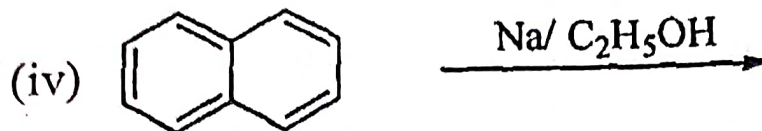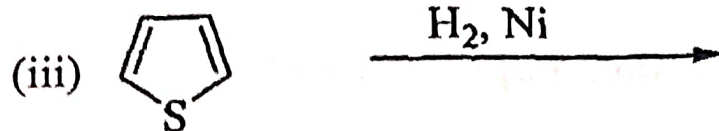## Instructions for Candidates

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

2.   Attempt any **six** questions.
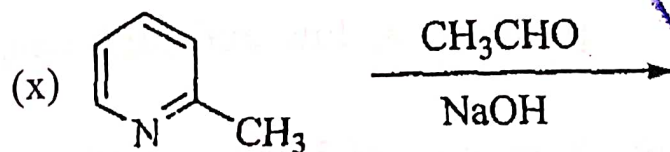
3.   **All** questions carry equal marks.
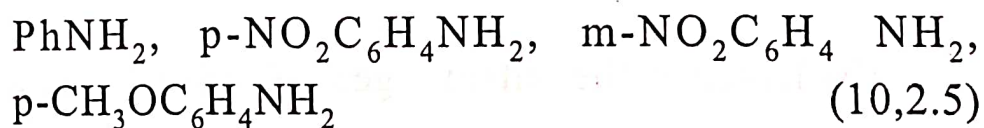
1.   (a) Complete the following reactions :

(i)    $\xrightarrow{\text{CrO}_3/\text{ AcOH}}$

(ii)    $\xrightarrow[\text{NaOH}]{\text{ArN}_2{}^+\text{Cl}^-}$

P.T.O.

(iii) [thiophene structure] $\xrightarrow{\text{H}_2,\ \text{Ni}}$

(iv) [naphthalene structure] $\xrightarrow{\text{Na/ C}_2\text{H}_5\text{OH}}$

(v) [indole structure] $\xrightarrow[\text{Pyridine}]{\text{SO}_3}$

(vi) [quinoline structure] $\xrightarrow{\text{Alk. KMnO}_4}$

(vii) $CH_3CH_2CN$ $\xrightarrow{\text{C}_2\text{H}_5\text{O}^-}$

(viii) $CH_3NC$ $\xrightarrow[\text{2. H}_2\text{O, H}^+]{\text{1. CH}_3\text{MgBr}}$

(ix) [anthracene structure] + [maleic anhydride structure] $\xrightarrow{\text{Heat}}$

(x) [pyridine ring with 2-CH3 substituent] $\xrightarrow[\text{NaOH}]{\text{CH}_3\text{CHO}}$

(b) Explain the order of basicity of following anilines :

$PhNH_2$, $p\text{-}NO_2C_6H_4NH_2$, $m\text{-}NO_2C_6H_4\ NH_2$, $p\text{-}CH_3OC_6H_4NH_2$                                    (10,2.5)

2. (a) How will you carry out following conversions :

(i) Quinoline to 8-Hydroxyquinoline

(ii) Naphthalene to 1 -Naphthoic acid

(iii) β-Picoline to 3-Aminopyridine

(b) Give the Gabriel phthalimide synthesis and explain why neopentylamine and aniline cannot be prepared by it.                                    (9,3.5)

3. (a) Explain the following :

(i) Nitration and sulphonation reaction of furan are carried out under mild reaction conditions.

P.T.O.

(ii) Sulphonation of naphthalene gives different products at low and high temperatures.

(iii) Formation of 3-chloropyridine when pyrrole is heated with chloroform in presence of KOH.

(b) Discuss the advantages of Emde's modification over Exhaustive methylation using suitable example?                                    (9,3.5)

4.  (a) Explain the following :

(i) Pyridine undergoes nucleophilic sub reactions at C-2 or C-4. Explain.

(ii) Phenanthrene undergoes electrophilic substitution as well as addition reactions preferentially at C-9 and C-10 positions. Explain with the help of examples.

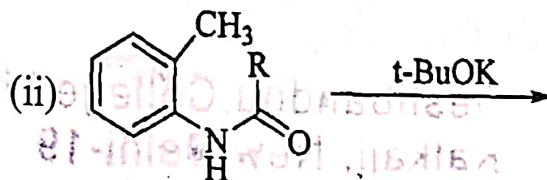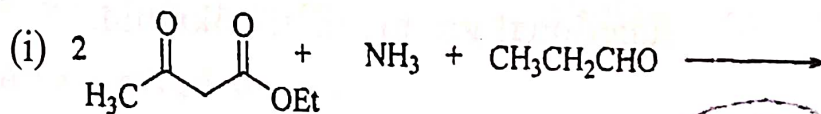(iii) Order of aromatic character: Pyrrole, furan, thiophene.

(b) Define 'Isoprene rule'. Mark out the isoprene units

with dotted lines and mention the class of terpenes to. which each one belongs to :
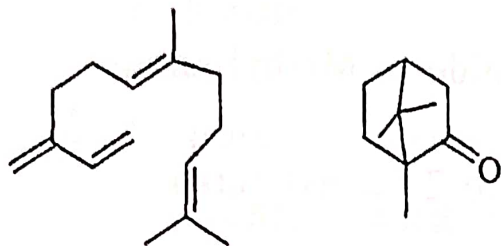


(9,3.5)

5. (a) Identify the product, reaction name and suggest the mechanism for the following reaction :

(i) 2  + NH$_3$ + CH$_3$CH$_2$CHO ⟶

(ii)  $\xrightarrow{\text{t-BuOK}}$

(c) How are primary, secondary and tertiary amines distinguished using Hinsberg test ? Give the relevant chemical reactions. (9,3.5)

6. (a) Suggest the best suitable reagent to bring out the following conversions :

(i) Pyrrole to pyrrole-2-aldehyde

(ii) Pyridine to n-Pentane

(iii) Acetamide to Methyl amine

(iv) Furan to 2-Phenyl furan

(b) How will you synthesize 2-Methyl quinoline by Skraup synthesis? Explain with the help of mechanism.

(c) How will you show the presence of the following functional groups in an alkaloid.

(i) O- Methyl group

(ii) -COOH group                                     (4,5,3.5)

7. (a) Write short note on (any TWO) :

(i) Reduction of nitrobenzene

(ii) Mannich Reaction

(iii) Pomeranz-Fritsch reaction

(b) Explain how can we synthesize 2,3,4,5-tetramethyl furan starting from acetoacetic ester.    (8,4.5)

8. (a) What happens when

   (i) Citral is treated with aq. Potassium carbonate

   (ii) Mixture of a methylamine and chloroform is treated with ethanolic potassium hydroxide

   (iii) Anthracene is treated with bromine in carbon tetrachloride.

   (b) How was the presence of pyrrolidine ring in nicotine proved by Karrer?

   (c) Electrophilic substitution in naphthalene is favored at 1-position. Explain.              (6,3,3.5)

9. (a) N-Ethyl-N-methylamine is chiral but non-resolvable however 2-aminobutane is resolvable. Explain.

   (b) Explain how the presence of two benzene rings fused together was confirmed in case of naphthalene.

P.T.O.

(c) Diazo coupling takes place either in mild acidic medium or mild alkaline conditions. Explain.

(d) Pyrrole behaves like phenol. Justify the statement using suitable examples.                    (3,3,3,3.5)

(14)   Your Roll No.2022

Sr. No. of Question Paper : 1387          A

Unique Paper Code          : 32171403

Name of the Paper          : Physical Chemistry – IV

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

Semester                   : IV

Duration : 3½ 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 **six** questions in all.

3.  Use of scientific calculator is permitted.

1.   (i)  Comment on the following :

     (a) Elementary reaction with molecularity greater than three are unknown.

     (b) In the steady state, the concentration of the reactive intermediate though small remains the same for an appreciable time.

                                        (2+2)

(ii) Predict the overall order of reaction for which half-life period depend inversely on the concentration and derive the expression for its half-life. (4)

(iii) The rate constant for a certain reaction is found to be tripled when the temperature is increased from 288K to 323K. If the enthalpy of reaction is 80 kJ/mol, calculate the activation energy of the reaction.

(4.5)

2.   (i) Differentiate the following **(any two)** :

   (a) Stationary and non-stationary chain reaction

   (b) Order and molecularity

   (c) Average rate and Instantaneous rate of reaction (2+2)

(ii) Under what conditions a given catalytic reaction may be classified into a general acid catalysis and a specific hydrogen-ion catalysis, if the acid catalysed reaction follows the mechanism :

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

$$SH^+ + H_2O \overset{k_2}{\longrightarrow} P + H_3O^+$$
(4)
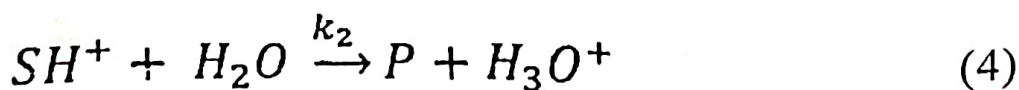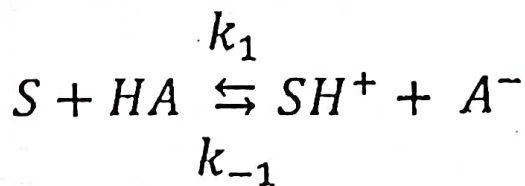
(iii) Derive the Michaelis - Menten equation for enzyme catalysed reactions. The mechanism involves the following steps :

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

$$ES \overset{k_2}{\longrightarrow} P + E$$
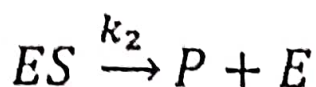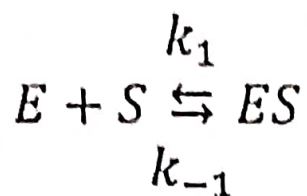
Show that the enzyme catalysed reaction is first-order and zero-order with respect to S at low and high concentrations of S, respectively.

(4.5)

3. (i) Explain the role of catalyst with the help of potential energy diagram? (4)

(ii) Hydroxide ion is involved in the mechanism but not consumed in this reaction in aqueous solution.

$$OCl^-(aq) + I^-(aq) \overset{OH^-}{\longrightarrow} OI^-(aq) + Cl^-(aq)$$
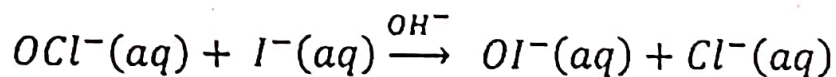
(a) From the data in the table, determine the order of reaction with respect to $OCl^-$, $I^-$, and $OH^-$, and the overall order.

P.T.O.

| $[OCl^-]$ /(M) | $[I^-]$/ (M) | $[OH^-]$ /M | Rate of formation of $OI^-$ (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 0.004 | 00.0020 | 1.00 | $4.8 \times 10^{-4}$ |
| 0.002 | 00.0040 | 1.00 | $5.0 \times 10^{-4}$ |
| 0.002 | 00.0020 | 1.00 | $2.4 \times 10^{-4}$ |
| 0.002 | 00.0020 | 0.50 | $2.4 \times 10^{-4}$ |
| 0.002 | 00.0020 | 0.25 | $9.4 \times 10^{-4}$ |

(b) Write the rate law. (4)

(iii) The following mechanism has been suggested for the decomposition of $O_3$

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O_3 + O \overset{k_2}{\rightarrow} 2O_2$$
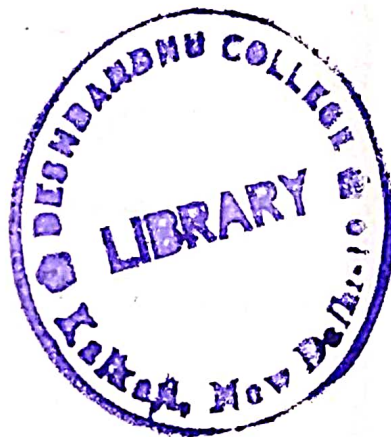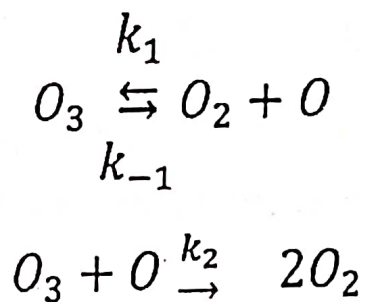
(a) Assuming $k_{-1}[O_2] > k_2[O_3]$, show that the rate of the all-overall reaction is

$$-\frac{d[O_2]}{dt} = \frac{k[O_3^2]}{[O_2]} .$$

(b) What could be concluded from the appearance of $\frac{1}{[O_2]}$ in the rate equation?

(4.5)

4. (i) Derive the relation between Arrhenius activation energy $E_a$ and the minimum energy $E_0$ of the collision theory of bimolecular reaction theory.

(4)

(ii) (a) What are the two conditions that are necessary for effective collisions?

(b) Why the value of steric factor p is usually less than 1 ?

(2+2)

(iii) Show that for a first order reaction, the time required for 99.9% completion of the reaction is 10 times the time for 50.0% completion.

(4.5)

5. (i) Write a short note on **any three** :
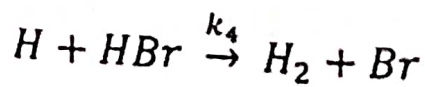
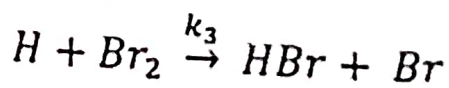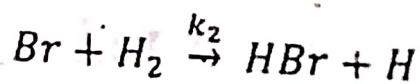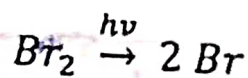(a) Effect of temperature on Photochemical Reactions

(b) Activated Complex Theory

(c) Conductometric titration of mixture of HCl and $CH_3COOH$ against NaOH

(d) Kohlrausch Law of Independent Migration of Ions

(3×3)

(ii) Why does the transport number of $Cd^{2+}$ ions in concentrated solutions of $CdI_2$ is negative?

(3.5)

6.   (i) State and derive Lambert-Beer's Law.

(4)

(ii) $2.0 \times 10^{-3}$ m thickness of a certain glass transmits 10% of the incident light of wavelength 300 nm. What percentage of light of the same wavelength will be absorbed by a $1.0 \times 10^{-3}$ m thickness of the glass?

(4)

(iii) The proposed mechanism of photochemical reaction between $H_2$ and $Br_2$ is

$$Br_2 \xrightarrow{h\nu} 2\,Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$H + HBr \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$
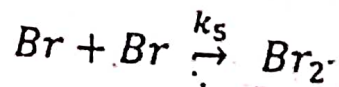
Derive the quantum yield of reaction.      (4.5)

7.   (i) Explain, giving reasons : **(any two)**

(a) Specific conductance decreases while equivalent conductance increase on dilution.

(b) Molar conductance values for alkali metal cations are in the order $Rb^+ > K^+ > Na^+ > Li^+$.

(c) ADC current cannot be used for conductance measurements. (2+2)

(ii) What are the various factors affecting the conductance of a solution? How do you account for the increase in conductance of solutions at high field strength and at high frequency?

(4)

(iii) A conductance cell when filled with 0.05 M solution of KCl records the resistance of 410.0 ohm at 25°C. When filled with $CaCl_2$ solution (11g $CaCl_2$ in 500 mL) it records 990 ohm. If the specific conductance of 0.05 M KCl solution is 0.00189 mho/cm, calculate (a) Cell constant, (b) specific conductance and (c) Molar conductance of $CaCl_2$. (4.5)

8. (i) Discuss (any two) applications of conductance measurements :

(a) Solubility and solubility product of a sparingly soluble salt.

(b) Determination of Ionic product of water.

(c) Degree of hydrolysis and hydrolysis constant of a hydrolysable salt. (4+4)

(ii) A solution of HCl acid is electrolysed in a transport cell using platinum electrodes. 20.175 g of the cathode solution contained 0.175g of Cl⁻ ion before electrolysis and 18.466 g of the cathode solution contained 0.146 g Cl⁻ ion after electrolysis. A silver coulometer connected in series had a deposit of 0.2508 g Ag. Calculate the transport number of Cl⁻ and H⁺ ions.

(4.5)

9. (i) Describe Hittorf's method or Moving boundary method employed in determining the transport number of an ion. (4)

(ii) Which of the following pairs will have higher molar conductance and why?

(a) LiCl or NaCl

(b) Cl⁻ ion in HCl or in NaCl (2+2)

(iii) The resistance of a 0.02 mol/dm³ solution of acetic acid in a cell having cell constant 0.2063 cm⁻¹ was found to be 888ohm. What is the degree of ionization of the acid at this concentration? (Given $\Lambda^0_m$ for acetic acid = 387.9 × 10⁻⁴ Smol⁻¹m²). (4.5)