Instructions for students

- Write your Name and Roll No. at the top of the first pages of all problems.
- This examination paper consists of 30 pages of problems including answer boxes.
- Total marks for INChO 2012 paper are 100.
- You have 3 hours to complete all the problems.
- Request the supervisor to provide you with blank pages for rough work.
- **Use only a pen to write the answers in the answer boxes. Anything written by a pencil will not be considered for assessment.**
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- You must show the main steps inthe calculations,
- Use only a non-programmable scientific calculator.
- For objective type question, mark **X** in the correct box. Some of the objective questions may have more than one correct answer.
- Values of fundamental constants required for calculations are provided on page 4.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.
- Do not leave the examination room until you are directed to do so.
- The question paper will be uploaded on the HBCSE website by 1st February 2012.

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Fundamental Constants

Avogadro number	$N_A = 6.022 \times 10^{23}\ mol^{-1}$
Electronic charge	$e = 1.602 \times 10^{-19}$ C
Molar gas constant	$R = 8.314\ J\ K^{-1}mol^{-1}$
	$= 8.314\ K\ Pa.dm^3\ K^{-1}mol^{-1}$
	$= 0.082\ L.atm\ K^{-1}mol^{-1}$
1 atomic mass unit (1u)	$= 931.5\ MeV/C^2$
1 eV	$= 1.602 \times 10^{-19}$ J
Rydberg constant	$R_H = 2.179 \times 10^{-18}$ J
Mass of electron	$m_e = 9.109 \times 10^{-31}$ kg
Plancks constant	$h = 6.625 \times 10^{-34}$ Js
Speed of light	$c = 2.998 \times 10^8\ ms^{-1}$
Acceleration due to gravity	$g = 9.8\ ms^{-2}$
Density of mercury	$= 13.6 \times 10^3\ kg\ m^{-3}$
Faraday constant	F = 96485 C

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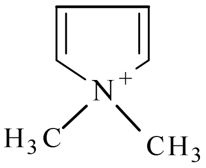
Name of Student **Roll No.**

Problem 1 18 marks

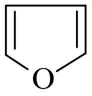
Heterocyclic compounds

A. Heterocyclic compounds occupy an important status in organic chemistry. Many of them have important biological properties. They can be aromatic or non-aromatic. Due to the presence of atoms other than carbon in them, they differ markedly from carbocyclic aromatic compounds.

1.1 Among the heterocyclic compounds listed below, the compound/s that is/are aromatic in nature is/are



A



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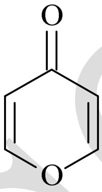
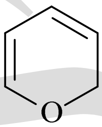


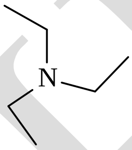
C



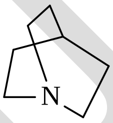
D

(2 marks)

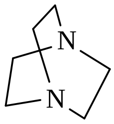
1.2 Arrange the following heterocyclic compounds in the order of decreasing reactivity with CH_3I.



E



F



G

(1 mark)

Aziridine, a nitrogen containing heterocyclic compound, can function as a nucleophile. It undergoes different reactions with acetyl chloride depending on the conditions.

1.3 Draw the structures of the isolable products **H** and **I**.

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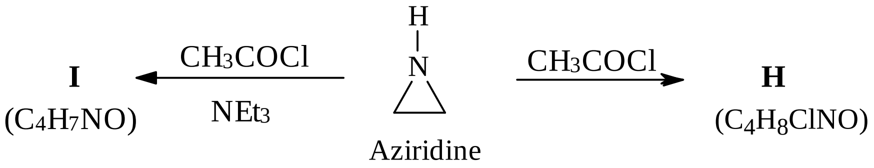


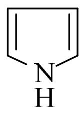
I

H

(2 marks)

B. Pyrroles are five membered nitrogen containing heterocyclic compounds present in ‘heme’ which is a constituent of hemoglobin.

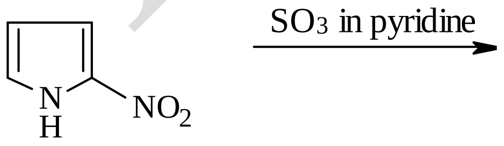
1.4 a) Draw all the significantly contributing resonance structures of pyrrole (**K**).



K

(2 marks)

b) Draw the major product of the following reaction



(1 mark)

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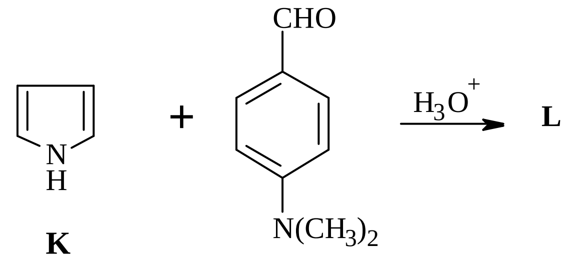
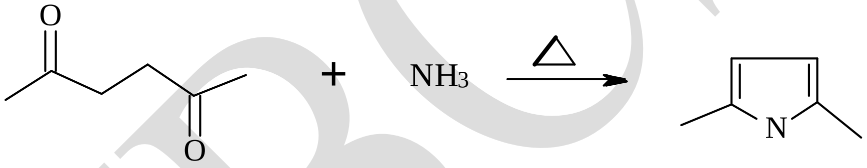
1.5 Pyrrole on reaction with 4-(N,N-dimethylamino) benzaldehyde in an acidic medium yields a deep coloured product **L** ($C_{13}H_{15}N_2$). Draw a possible structure of **L.**



L

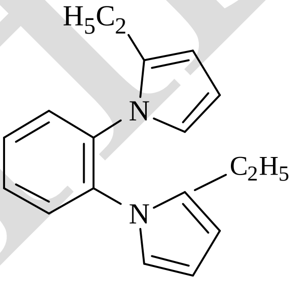
(2 marks)

Paal-Knorr synthesis is one of the commonly used methods to prepare pyrrole and its derivatives. One example is illustrated below.



2,5 - dimethylpyrrole

1.6 Identify the starting compounds and their molar ratio required for the synthesis of compound **J**.



J

(2 marks)

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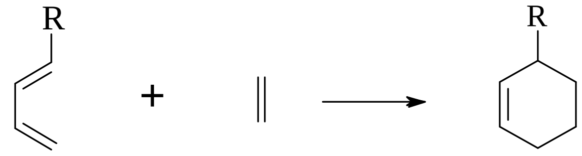
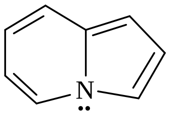
C. A cycloaddition reaction is one in which two reactants containing multiple bonds add together to give a cyclic product. In such a reaction the terminal ends of the reacting parts of the two reactants join each other. Diels-Alder reaction is an example of [4+2] cycloaddition, where 4 and 2 indicate the π-electrons in the two reactants, as shown below.



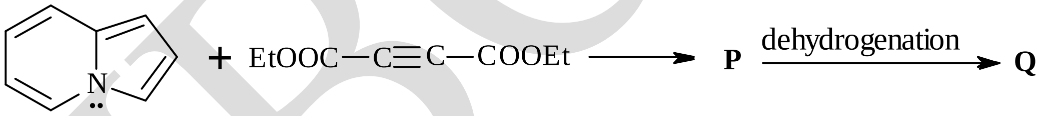
Heterocyclic compounds with N atom at a ring junction are also known. One such compound is indolizine (**M**).



M

Indolizine undergoes a [8+2] cycloaddition reaction with diethyl acetylene dicarboxylate to give **P** which on dehydrogenation with Pd gives compound **Q**.

1.7 Draw the structures of **P** and **Q**.



P

Q

(2 marks)

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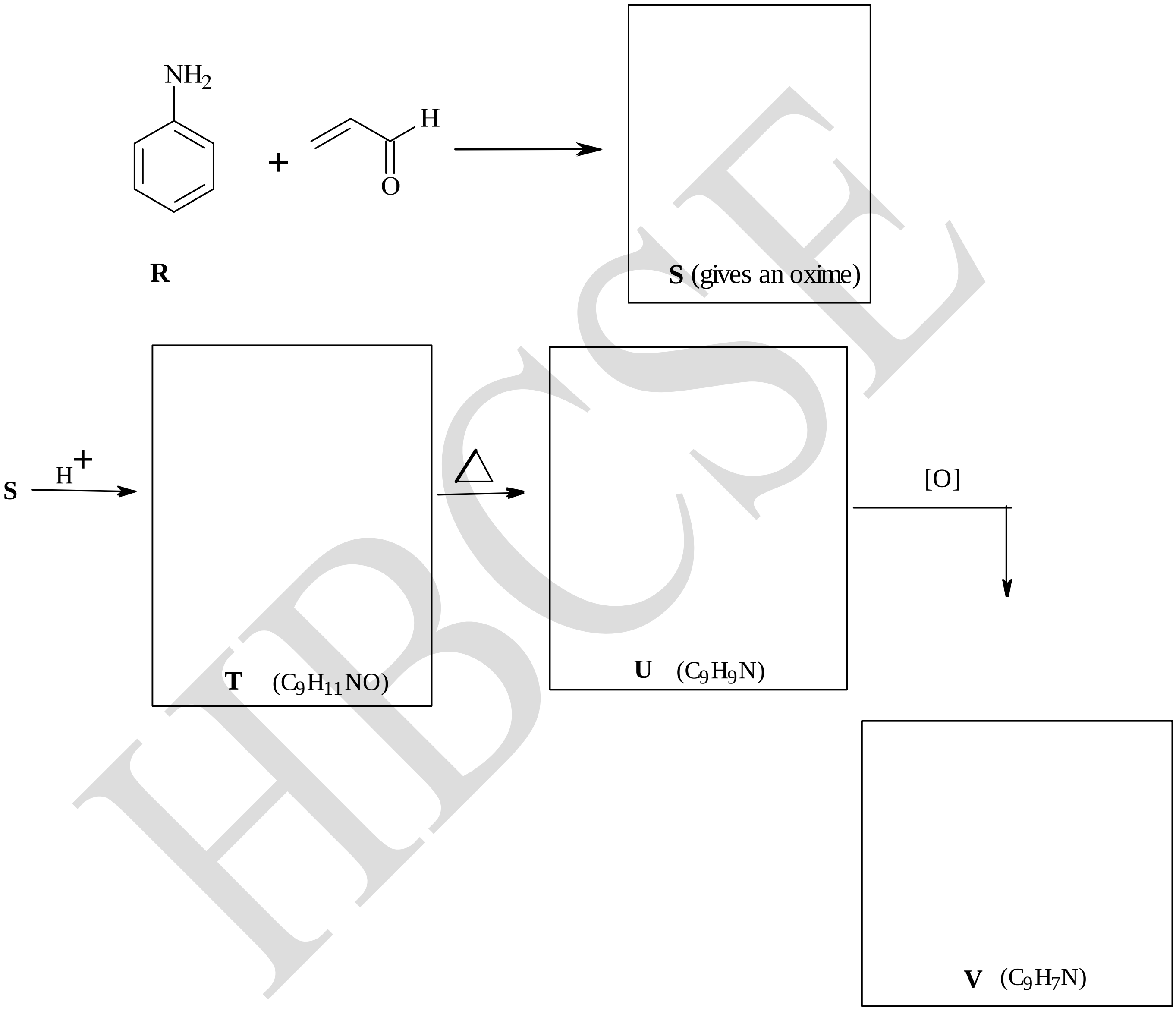
1.8 Is **Q** aromatic?

Yes ☐ No ☐

(1 mark)

A very useful heterocyclic compound **V** is prepared by the following synthesis.

1.9 Draw structures of the intermediates **S, T, U** and of **V**.



(3 marks)

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Problem 2 **12 marks**

Analysis of alloys

Alloys are materials with specific properties that are obtained by combination of different metals in definite proportions. Both conventional and modern techniques are used for the determination of the chemical composition of an alloy. This question deals with different methods that are used to determine the composition of a copper-zinc-lead alloy.

A.

Iodometric method is one of the conventional methods used for the estimation of copper content of an alloy. In this method, the alloy sample is first dissolved in nitric acid, evaporated to dryness and then extracted with dilute sulphuric acid. In one such analysis, 0.685 g of an alloy sample was treated with acid and diluted to 250 mL **(solution A).** 10 mL of **solution A** was used for the estimation of copper iodometrically. For this titration, an excess of solid potassium iodide was added to 10 mL of **solution A** which was preadjusted to an optimum pH. The liberated I_2 was titrated with sodium thiosulphate solution.

2.1 Write the balanced equations of the reactions involved in

i) reaction of Cu(II) with iodide and

ii) the titration.

(1.5 marks)

2.2 The volume of thiosulphate required for the titration was 6.1 mL. The strength of supplied aqueous thiosulphate solution was expected to be 0.05 M. Calculate the amount of copper in grams and the percentage of copper in the alloy sample.

(1.5 marks)

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However, thiosulphate is not a primary standard and needs to be standardized to know its exact molarity. The above thiosulphate solution was standardized using 0.0125 M potassium dichromate solution. For this purpose, excess of solid potassium iodide was added to 10 mL of potassium dichromate solution in an acidic medium and the liberated iodine was titrated with the thiosulphate solution.

2.3 Write the balanced equation of the reaction between dichromate and iodide**.**

(1 mark)

2.4 The observed reading in the above titration was 15.5 mL. Calculate the exact molarity of the thiosulphate solution.

(1 mark)

2.5 Using the molarity calculated by you, recalculate the amount of copper in grams present in the alloy sample. Calculate the relative percentage deviation for the copper content obtained in **2.2**.

(1 mark)

B.

Another method used to analyze a copper-zinc-lead alloy is electrolysis. In this method, the alloy sample is dissolved in nitric acid of suitable strength. In the presence of nitric acid, the lead present in the alloy is quantitatively oxidized to lead dioxide and deposited on the anode. In the process, the nitrate ions are reduced to NH_4^+ which prevents liberation of hydrogen at the cathode.

2.6 Write the balanced equation for the reaction representing the reduction of nitrate ions to ammonium ions.

(1 mark)

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2.7 Write balanced equation of the reaction of formation of PbO_2 at the anode.

(0.5 mark)

0.685g of copper-lead-zinc alloy containing 1% lead [w/w] was dissolved in nitric acid and diluted to 250cm^3 [**solution B**]. 100 mL of **solution B** was electrolyzed with a current of 1.47 mA for 1 hour and 20 minutes. This ensured that lead was completely converted to dioxide.

2.8 Calculate the millimoles of lead dioxide formed.

(1 mark)

2.9 Calculate the fraction of the total current passed that is used in the formation of PbO_2.

(1 mark)

C.

The zinc content in the alloy can be determined by an instrumental technique called Fluorimetry. This technique is based on the measurement of the intensity of the fluorescent radiation produced, which is directly proportional to the concentration of the species producing fluorescence. The reagent that is used for the determination of zinc by flourimetry is oxine. By itself, it does not show fluorescence, whereas zinc-oxine complex shows fluorescence. In such determinations fluorescence of the sample solution is measured first and then a standard zinc solution of known concentration is added to a definite volume of the sample solution. The fluorescence of the resulting solution is then measured. This technique is known as standard addition method.

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2.10 The solution in **2.8,** after the electrolysis (that is, after deposition of PbO_2) was evaporated to dryness and extracted with dil. sulphuric acid and diluted to 100 mL (**solution C).** 10 mL of **solution C** was further diluted to 100 mL (**solution D**). 1.0 mL of **solution D** was used for the fluorimetric determination of zinc. The data obtained is presented below,

Vol of sample solution **D** (mL)	Vol of oxine solution added (mL)	Vol of 1ppm Zn added (mL)	Total volume in mL	Fluorescence intensity
1.0	0.5	----------------------------	50	25
1.0	0.5	1.0	50	42

From this data, calculate the amount of zinc in whole of **Solution B**, (**2.8**) and the percentage of zinc in the alloy sample.

(2.5 marks)

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Name of Student

Problem 3 18 Marks

Halogens

The chemistry of halogens is interesting. Halogens belong to the group 17 of the periodic table. The name "Halogen" was introduced by J.S.C. Schweiggen in 1811 to describe the property of chlorine (at that time unique among the elements) to combine directly with metals to give salts. Iodine is an essential trace element for humans and plays an important role in growth regulating hormone thyroxine, which is produced in the thyroid gland. Deficiency of iodine in diet leads to Goitre. In order to prevent this condition, about 0.01% NaI is added to the table salt. Iodine is a lustrous solid and sublimes at ordinary temperature.

3.1 The sublimation of iodine is due to (Mark '**X**' in the correct box.)

(a) low melting point ☐

(b) weak I-I bond ☐

(c) weak van der Waals forces among I_2 molecules ☐

(d) lone pair - lone pair repulsion in I_2 molecule. ☐

(1 mark)

3.2 Iodine is a semiconductor under normal conditions (band gap ~ 1.3eV). However, on compression to about 350 kbar pressure, it becomes conducting. The change is due to (Mark '**X**' in the correct box/es.)

(a) formation of a partially filled band ☐

(b) change in electronic configuration ☐

(c) better overlap of molecular orbitals ☐

(d) high ionization potential ☐

(1 mark)

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3.3 Will chlorine on compression to the same pressure conduct electricity? (Mark '**X**' in the correct box.)

Yes ☐ No ☐ **(0.5 mark)**

Iodine is only slightly soluble in water (0.34g/kg at 25 °C). However, it is highly soluble in an aqueous solution containing iodide ions and also in organic solvents.

3.4 **(a)** The iodine containing species having maximum concentration, present in a 0.5 M KI solution containing 1.5 M I_2 is ☐

(1.5 marks)

(b) The solubility of iodine in carbon tetrachloride is due to

(i) ionic solvent-solute interaction ☐

(ii) charge-transfer phenomenon ☐

(iii) van der Waals interaction ☐

(iv) dissociation of iodine ☐

(0.5 mark)

(c) In an experiment, the solubility of iodine in diethyl ether**,** n-hexane, carbon tetrachloride and toluene was measured. The solubilities were: 337g/kg, 182g/kg, 19 g/kg and 13 g/kg. Correlate the solubilities with the solvents.

Solvent	**Solubility**	**Solvent**	**Solubility**
Carbon tetrachloride		n-Hexane	
Diethyl ether		Toluene	

(1.5 marks)

Colour of iodine solution is sensitive to the nature of the solvent. Iodine is dissolved in two solvents; diethyl ether and carbon tetrachloride. The colours of the two solutions are bright violet and deep brown. The λ_{max} values recorded were 460 – 480 nm and 520 – 540 nm.

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3.5 Correlate solvents with the λ_{max} and the colour.

Solvent	**λmax**	**Color**
Carbon tetrachloride		
Diethyl ether		

(2 marks)

Interhalogen compounds are interesting compounds. Fluorine is the most reactive halogen. Bromine exhibits formal oxidation states of +1, + 3 and +5 in its interhalogen compounds. Fluorine reacts with bromine in gas phase to form compound **A** (with about 20% fluorine by weight) which at room temperature disproportionates to compound **B**.

3.6 Write the balanced equations for the two reactions leading to **A** and **B.**

(2 marks)

Compound **B** is a liquid at room temperature (b.p.126°C). It is not only a fluorinating agent, but also a preparative nonaqueous solvent. Antimony (V) fluoride dissolves freely in **B** to form a complex **(C)**.

3.7 Write the equation for the formation of **C**.

(1 mark)

3.8 Identify the Lewis acidic and Lewis basic species in the reactants and products in the equation written in **3.7**.

	Lewis Acid	**Lewis Base**
Reactants		
Products		

(2 marks)

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Trifluorosulfur nitride (SNF_3) is prepared by the reaction of S_4N_4 with AgF_2 in hot CCl_4.

3.9 a) The central atom in SNF_3 is

b) Draw the Lewis dot structure of SNF_3, consistent with VSEPR.

c) The total number of electrons in the valence shell of the central atom is

d) Geometry around central atom is

(3 marks)

3.10 Draw the structure of $(Sb_2F_{11})^-$ species.

(1 mark)

3.11 Out of the species PO_4^{3-}, SO_4^{2-}, IO_4^- and XeO_6^{4-}, the most oxidizing one is

(1 mark)

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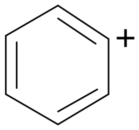
Name of Student **Roll No.**

Problem 4 23 marks

Chemistry of carbocations

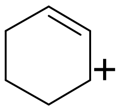
Carbocations are intermediates having a positively charged carbon atom. They are formed in a variety of chemical reactions including synthesis of natural products.

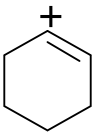
4.1 In the following carbocation, hybridization of the positively charged carbon is

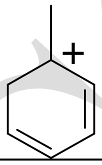


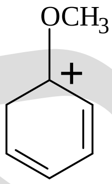
(1 mark)

4.2 List the following carbocations in the order of decreasing stability.









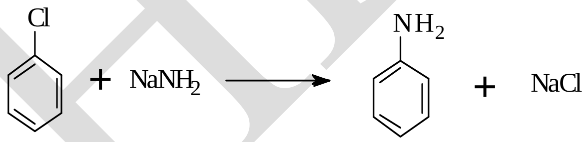
I **II** **III** **IV** **(1 mark)**

4.3 State whether the following conversions can proceed through carbocation intermediate or not. (Mark **X** in appropriate box)

i)

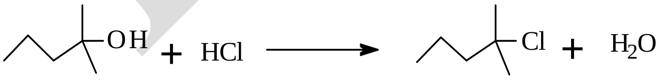
Yes ☐ No ☐

ii)



Yes ☐ No ☐

iii)



Yes ☐ No ☐

(3 marks)

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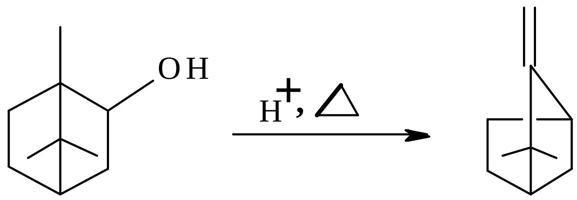
Carbocations formed in reactions frequently undergo rearrangements to give more stable species. One such example is shown below



A **B**

4.4 In the conversion of **A** → **B,** draw the structure of the carbocation (**C**) formed initially.

C

(1 mark)

4.5 Carbocation **C** undergoes a rearrangement to form a more stable carbocation (**D**). Draw the structure of **D**.

D

(1 mark)

4.6 The species that is eliminated from **D** to form **B** is

(i) hydride ion ☐

(ii) methyl group ☐

(iii) proton ☐

(iv) water ☐ **(1 mark)**

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4.7 Compound **B** is

(i) monocyclic ☐

(ii) bicyclic ☐

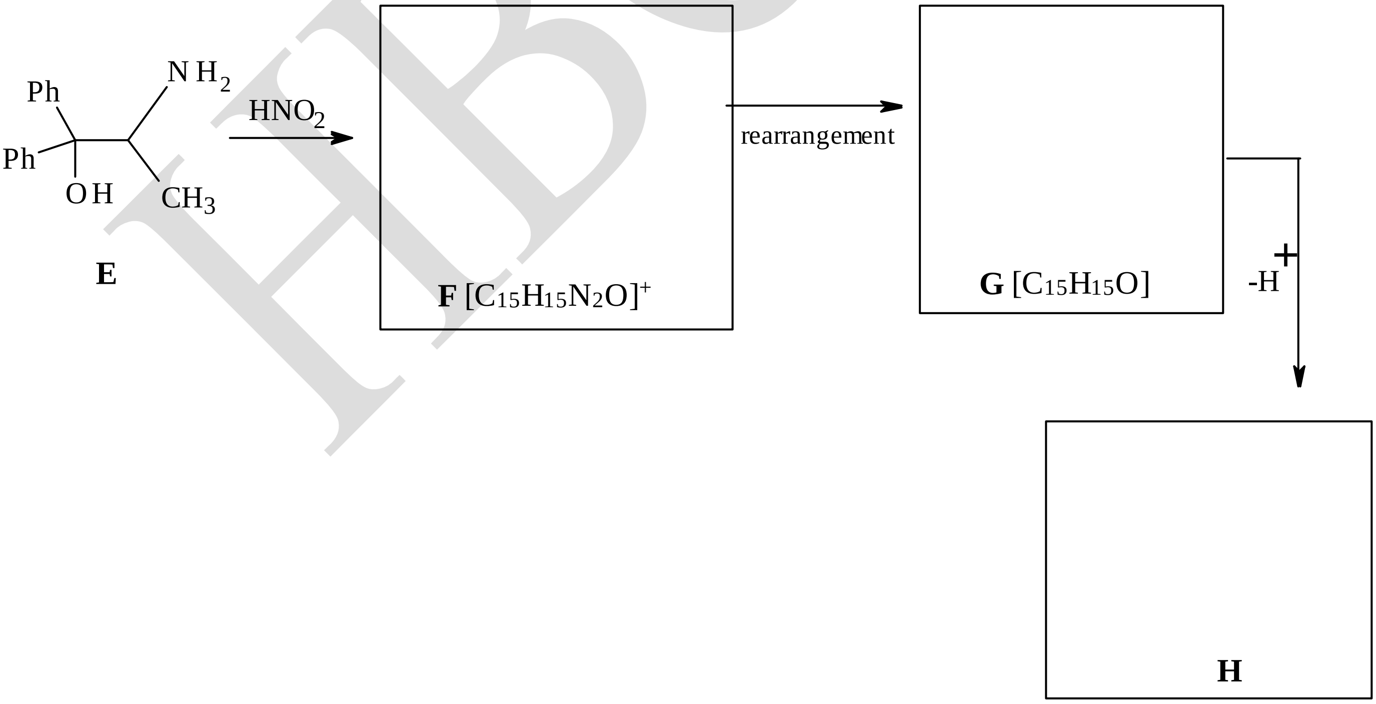
(iii) tricyclic ☐

(iv) tetracyclic ☐ **(1 mark)**

4.8 The structure of the product formed when **B** reacts with HBr in the presence of a peroxide is

(1 mark)

4.9 Carbocations can be prepared by a number of ways. One such reaction sequence which involves a carbocation formation and a rearrangement is presented below. Draw the structures of **F**, **G** and **H**.



(3 marks)

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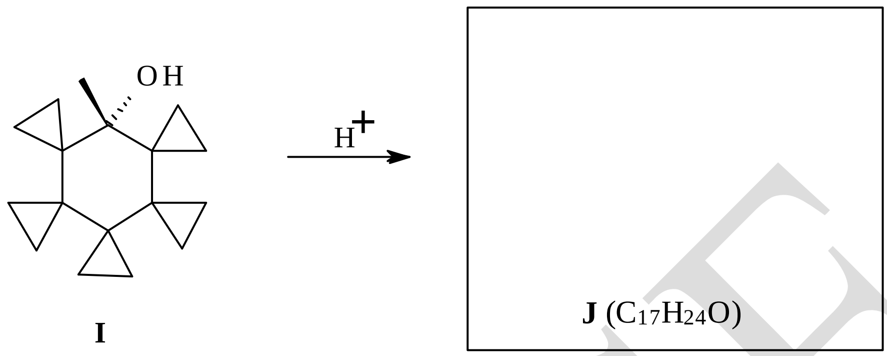
4.10 In the reaction of some molecules the carbocation initially formed undergoes a series of sequential rearrangements to form a product. **I** is one such substrate.

Draw the structure of the product **J** obtained when **I** undergoes sequential rearrangements on treatment with a Bronsted acid.

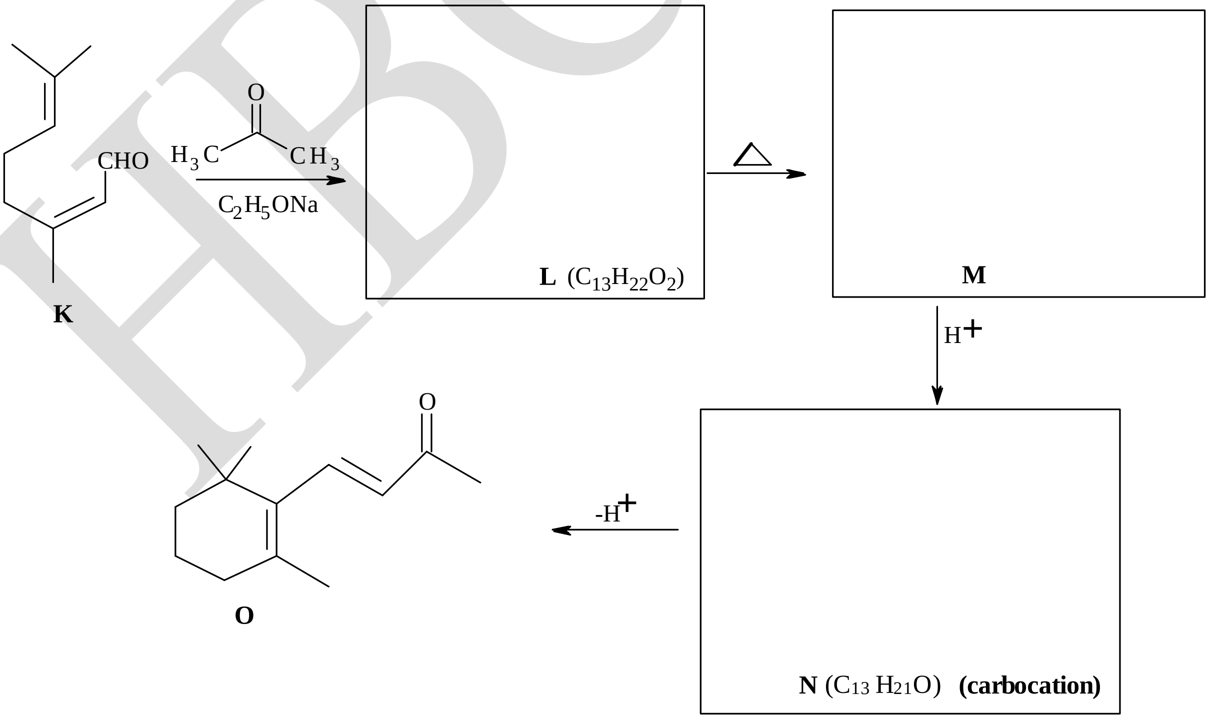


I

(2 marks)

Terpenes are natural products obtained from plants. Terpene **K**, a constituent of lemon grass oil, is used in the synthesis of compounds which find applications in perfumes. This synthesis involves a carbocation intermediate.

4.11 Complete the following sequence for synthesis of **O** by drawing the structures of **L**, **M** and **N**. (**L** consumes two equivalents of bromine)



K

O

(3 marks)

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4.12 In this synthesis an appreciable amount of another product **P**, which is a positional isomer of **O,** is also formed. Draw the structure of **P**.

P

(1 mark)

4.13 The number of stereoisomers possible for compound **O** is

(i) 2 ☐

(ii) 4 ☐

(iii) 6 ☐

(iv) 8 ☐

(1 mark)

4.12 The number of optical isomers for compound **P** is

(i) 2 ☐

(ii) 4 ☐

(iii) 6 ☐

(iv) 8 ☐

(1 mark)

4.13 Structure determination of alkenes involves the use of ozonolysis. Draw the structure/s of products obtained on ozonolysis of **O**.

(2 marks)

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Name of Student **Roll No.**

Problem 5 18 marks

The 'light' side of chemistry

A. Many chemical reactions can be brought about by the absorption of light of suitable wavelength. Such reactions are known as photochemical reactions. In a photochemical reaction, only the first step is photochemical and the rest are thermal. The energy of the absorbed photon is used for the chemical conversions.

For the photochemical combination of hydrogen and chlorine to form hydrogen chloride, the following mechanism was suggested.

$$Cl_2 \xrightarrow{(h\nu)} 2Cl^\bullet \ldots\ldots\ldots\ldots\ldots\ldots\ldots (i)$$

$$Cl^\bullet + H_2 \xrightarrow{k_1} HCl + H^\bullet \ldots\ldots\ldots\ldots (ii)$$

$$H^\bullet + Cl_2 \xrightarrow{k_2} HCl + Cl^\bullet \ldots\ldots\ldots\ldots (iii)$$

$$2Cl^\bullet \xrightarrow{k_3} Cl_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (iv)$$

5.1 For the sequence presented above, Identify the chain propagation and chain termination step/s. (Write the appropriate reaction number)

Propagation step:

Termination step:

(1.5 marks)

To simplify complex rate equations, one of the approximation methods used is steady state approximation. According to this concept, if a reaction involves a highly reactive intermediate 'X', after a short span of time, 'X' reaches a 'steady state'. Under steady state, the rate of formation of X = rate of consumption of X. It is called as steady state because concentration of X remains constant at steady state.

In the above photochemical reaction, one photon of absorbed light converts one molecule of Cl_2 to Cl radicals. This step is temperature independent and hence the rate of this step depends only on the intensity of light absorbed, I_{abs}.

5.2 Assuming $H^\bullet$ and $Cl^\bullet$ to be under steady state, derive the expressions for

i) $\frac{d[H^\bullet]}{dt}$ ii) $\frac{d[Cl^\bullet]}{dt}$ in terms of rate constants and I_{abs}

iii) $[H^\bullet]$ in terms of $I_{abs}, [Cl_2]$ and rate constants.

HBCSE

(3.5 marks)

5.3 Derive the expression for $\frac{d[HCl]}{dt}$ in terms of I_{abs} and $[H_2]$.

(1.5 marks)

5.4 One mole of photons is known as one Einstein of radiation. According to Stark-Einstein law of photochemical equivalence, one mole of reactant absorbs one Einstein of energy. For a photochemical reaction, a term called 'quantum yield' is defined as

$$\text{Quantum yield } (\phi) = \frac{\text{No. of moles of reactant converted}}{\text{No. of Einstein absorbed}}$$

The correct statement/s is/are

i) For a chain reaction $\phi_{gas} >> \phi_{solution}$ ☐

ii) In a photochemical chain reaction $\phi >> 1$ ☐

iii) In a photochemical chain reaction $\phi << 1$ ☐

iv) For a chain reaction $\phi_{gas} << \phi_{solution}$ ☐

(2 marks)

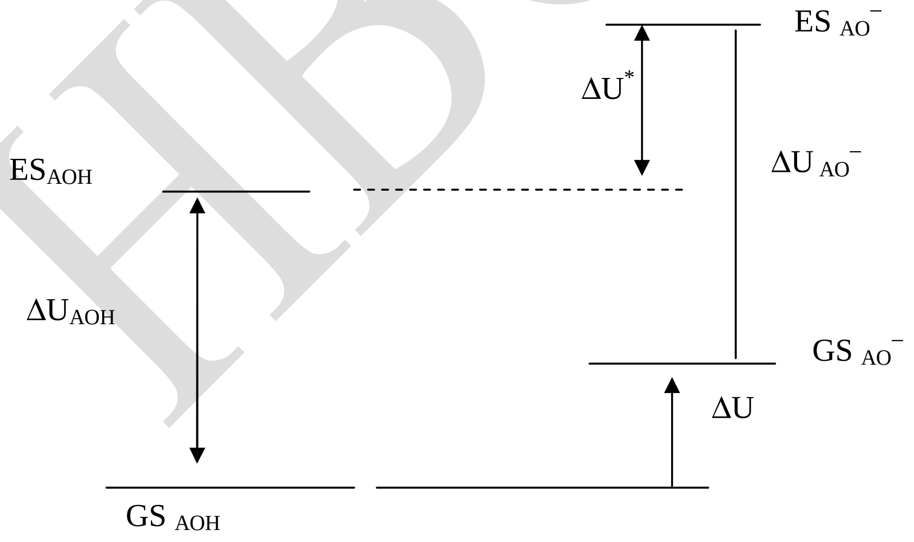
HBCSE

5.5 In the photochemical reaction of H_2 and Cl_2, Cl_2 absorbs at wavelength of 488 nm. When the Cl_2 gas is irradiated with a 60 watt lamp that emits radiation with 80% efficiency, 4.1 mmol of HCl were formed in 10 sec. Calculate the quantum yield for the reaction.

(3 marks)

B.

2-Naphthol (AOH) in solution can lose a proton to water molecule and thus acts as an acid. It is in equilibrium with its conjugate base (AO^-). The dissociation constant for this equilibrium depends on whether, 2-naphthol is in the ground state or its first electronically excited state. The excitation of 2-naphthol can be brought about by absorption of light. Consider the energy level diagram presented below.



The energies of the ground (GS) and excited (ES) states of AOH and AO^- are represented in the diagram, and the symbol ΔU (without and with different labels) indicates units of energy per mole.

HBCSE

5.6 a) If ν_{AOH} and ν_{AO^-} are the frequencies of light absorbed by AOH and AO^- respectively. Write the expressions for ΔU_{AOH} and ΔU_{AO^-} in terms of ν_{AOH} and ν_{AO^-} and Avogadro's number N_A.

(1 mark)

b) From the energy level diagram, deduce ΔU^*,

(1 mark)

c) In this case, it can be assumed that $\Delta U \approx \Delta H$. Deduce the expression for $(\Delta H - \Delta H^*)$ in terms of ν_{AOH} and ν_{AO^-} .

(1.5 marks)

5.7 Assume that the entropy difference (ΔS) between the ground and the excited states of AOH and that of AO^- are the same. Let pk_a and pk_a^* be the dissociation constants of AOH in ground state & excited state respectively.

a) Deduce the expression for Δpk_a $(pk_a^* - pk_a)$ in terms of ν_{AOH} and ν_{AO^-}.

(2 marks)

b) If ν_{AO^-} and ν_{AOH} are 85×10^{13} Hz and 90×10^{13} Hz respectively. Calculate Δpk_a of 2-naphthol at 300K.

(1 mark)

HBCSE

Name of Student	**Roll No.**

Problem 6 **11 marks**

Acids, bases and buffers

A. A buffer is a solution of weak acid and its conjugate base or a weak base and its conjugate acid. It resists the change in pH, when small amount of strong acid or base is added to it. Buffer solutions have wide applications.

6.1 HCl gas is passed through an aqueous solution of 0.1M 1-aminopropane ($PrNH_2$) till the pH reaches 9.71. Calculate the ratio of $[PrNH_2] / [PrNH_3^+]$ in this solution. $[K_a (PrNH_3^+) = 1.96 \times 10^{-11}]$.

(1.5 marks)

6.2 0.4 g of solid NaOH is added to 1L of the above buffer solution. Calculate the pH of the resulting solution.

(2 marks)

HBCSE

6.3 20.0 mL of 0.10 M of 1-aminopropane is titrated with 0.10 M of HCl. Calculate the pH at the equivalence point and hence select the appropriate acid-base indicator from **Table 1.**

Table 1: List of acid/base indicators

Common name	**Transition range, pH**	**Color change**
Methyl orange	3.2 - 4.4	red-orange
Methyl red	4.2 - 6.2	red-yellow
Phenol red	6.8 - 8.2	yellow-red
Phenolphthalein	8.0 - 9.8	colorless-red
Thymolphthalein	9.3 - 10.5	colorless-blue

(1.5 marks)

HBCSE

B.

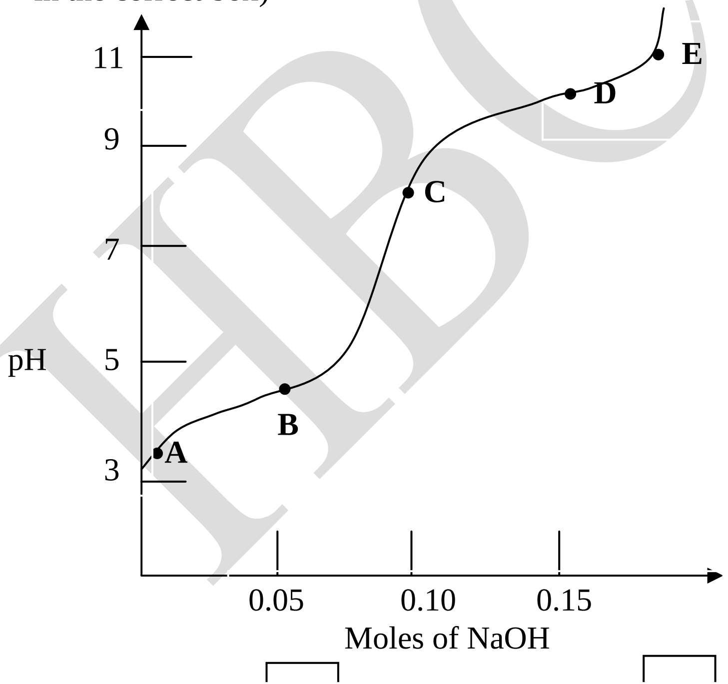
6.4 4-aminobutanoic acid is an important neurotransmitter. It plays a role in regulating neuronal excitability throughout the nervous system.

(pK$_{a2}$ = 10.70) (pK$_{a1}$ = 4.82)

Draw all the possible structures of the above amino acid that can exist in an aqueous solution at different pH.

(1 mark)

6.5 A pH titration curve for 0.10 M 4-aminobutanoic acid hydrochloride solution against NaOH is shown below. Select the buffer region/s in the following titration. (Mark **X** in the correct box)



around point **A** ☐ around point **B** ☐ around point **C** ☐

around point **D** ☐ around point **E** ☐

(1.5 marks)

HBCSE

6.6 Calculate the ratio [H_2N-R-COO^-]/[H_3N^+-R-COOH], at pH 7.0, for 4-aminobutanoic acid (R = –$(CH_2)_3$–).

(2.5 marks)

Paper electrophoresis is a technique that is useful for separation of small charged molecules, such as amino acids. In this technique a strip of filter paper is moistened with a buffer and the ends of the strip are immersed into the buffer solution containing electrodes. The sample is spotted at the centre of the paper and a high voltage is applied. The compounds will migrate to respective electrodes according to their charges.

6.7 When 4-aminobutanoic acid is subjected to electrophoresis at pH 6.0, the molecules

(i) do not migrate. ☐

(ii) migrate towards the anode (+) ☐

(iii) migrate towards the cathode (–) ☐

(1 mark)

HBCSE