

**Indian National Chemistry Olympiad 2016**  
**Theory (3 hours)**

Name: \_\_\_\_\_

Class: \_\_\_\_\_ Board: \_\_\_\_\_

Roll No.     -     -    M/F: \_\_\_\_\_

I **permit/do not permit** (*strike out one*) HBCSE to make my INO academic performance and personal details public unless I communicate my consent in writing

**I have read the Procedural Rules of the INOs and agree to abide by them.**

Name of student: \_\_\_\_\_

Signature: \_\_\_\_\_ Place: \_\_\_\_\_ Date: January 30, 2016

Please Note:

- Fill out the top half of the Performance card. Make sure that the performance card is attached to the question paper.
- Do not detach the performance card.

*Do not write anything below this line*

Question No	1	2	3	4	5	Total
Marks	20	24	17	17	24	102
Marks Obtained						
Signature of Examiner						

**Instructions for students**

- Write your Name and Roll No. at the top of the first pages of all problems.
- This examination paper consists of **28** pages of problems including answer boxes.
- Kindly check that the booklet has all the pages.
- Total marks for INChO 2016 paper are **102**.
- You have 3 hours to complete all the problems.
- Blank space for rough work has been provided at the end of the paper.
- Use only a pen to write the answers in the answer boxes. Anything written by 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 in the 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 2.
- 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 on 2<sup>nd</sup> February 2016.

**Fundamental Constants**

Avogadro number  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Electronic charge  $e = 1.602 \times 10^{-19} \text{ C}$

Molar gas constant  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $= 8.314 \text{ K Pa} \cdot \text{dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$   
 $= 0.082 \text{ L} \cdot \text{atm K}^{-1} \text{ mol}^{-1}$

1 atomic mass unit (1u)  $= 931.5 \text{ MeV}/c^2$

1 eV  $= 1.602 \times 10^{-19} \text{ J}$

1  $\text{cm}^{-1}$   $= 11.9 \times 10^{-3} \text{ kJ mol}^{-1}$

Rydberg constant  $R_H = 2.179 \times 10^{-18} \text{ J}$

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

Planck's constant  $h = 6.625 \times 10^{-34} \text{ Js}$

Speed of light  $c = 2.998 \times 10^8 \text{ ms}^{-1}$

Acceleration due to gravity  $g = 9.8 \text{ ms}^{-2}$

Density of mercury  $= 13.6 \times 10^3 \text{ kg m}^{-3}$

Faraday constant  $F = 96485 \text{ C mol}^{-1}$

Temperature  $0^\circ\text{C} = 273.15 \text{ K}$

Name of Student

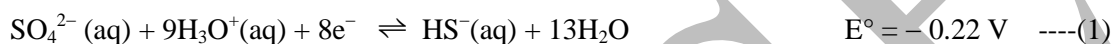
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**Problem 1**

**20 Marks**

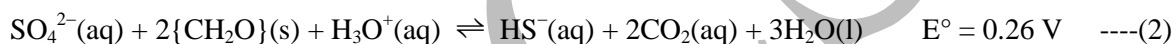
**Sulphate dynamics in Wastewaters**

Wastewaters are one of the highly complex chemical systems in our environment. Understanding these complex chemical reactions is important for safe management of wastewater systems. Here we look at some of the chemical dynamics of sulphate ions in wastewaters. Under scarcity of stronger oxidizers such as  $O_2$  and  $NO_3^-$ ,  $SO_4^{2-}$  ions can act as oxidizing agents for organic matter in wastewater aiding its decomposition. Sulphate reduction is often facilitated by sulphate-reducing bacteria (SRB), which are usually present in sewage and thrive in an anaerobic (low oxygen) environment. Sulphate reduction can eventually lead to production of toxic  $H_2S$  gas. The overall redox reaction can be represented by the equation:



$HS^-$  thus produced gets converted into  $H_2S$ .

In sewage, organic matter is present predominantly as suspended solid particles, which can be represented as  $\{CH_2O\}$ . This matter can act as food for SRB and as a reducing agent for sulphate. The chemical transformation in the process can be represented as



*For all parts in this problem, take temperature of the system to be 298 K.*

- 1.1 Determine the change in standard Gibbs free energy,  $\Delta G^\circ$ , for reaction (2) in kJ.

**(1 mark)**

- 1.2 Write an expression for equilibrium constant,  $K$ , for reaction (2) in terms of molar concentrations of the relevant chemical species.

**(1 mark)**

- 1.3 Calculate the value of  $K$  for reaction (2).

**(1 mark)**

- 1.4 A sewage entering a septic tank has  $[\text{SO}_4^{2-}] = 0.5 \text{ mM}$  and  $\text{pH} = 7.0$ . Assuming (2) to be the predominant redox reaction in the sewage, determine the concentration of dissolved  $\text{H}_2\text{S}$  in it when the system reaches equilibrium. (For  $\text{H}_2\text{S}$ ,  $\text{pK}_{\text{a}1} = 7.0$  and  $\text{pK}_{\text{a}2} = 11.96$ ).

Assume that

- $\text{H}_2\text{S}$  and  $\text{CO}_2$  gases produced remain in the solution phase.
- the carbonic acid produced here doesn't undergo dissociation.
- the sewage acts as buffer.

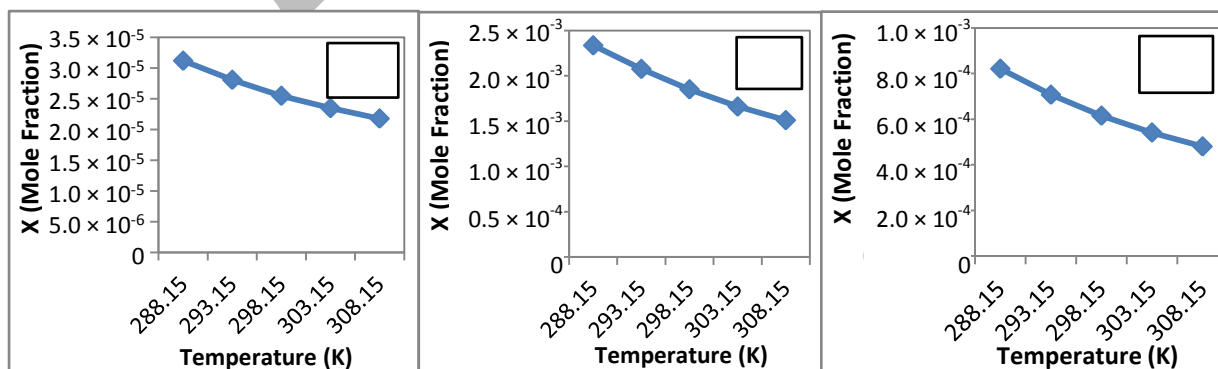


(2 marks)

Under aerobic conditions,  $\text{CH}_4$  is also often produced in the decomposition of sewage in addition to  $\text{H}_2\text{S}$  and  $\text{CO}_2$ .

- 1.5 Following graphs show temperature dependence of solubilities of the three gases in water, which includes the gas in dissolved form as well as its reaction products with water.

i) Label the boxes in each graph with appropriate gas.



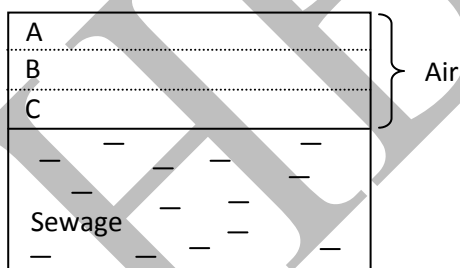
ii) Which of the three gases will escape from sewage the fastest?

(2 marks)

1.6 Septic tanks have a certain amount of air above the water level. In one such tank, the average composition of the air was found to be  $N_2 = 86\%$ ,  $O_2 = 9\%$ ,  $H_2O = 1.5\%$ ,  $CO_2 = 1.5\%$ ,  $H_2S = 1\%$  and  $CH_4 = 1\%$  (where the percentages are by mass). Calculate the average density of this air in  $kg\ m^{-3}$ , assuming its pressure to be 1 atm and all gases to be ideal.

(2 marks)

1.7 Unless there is turbulence or mixing, gases entering a chamber do not immediately diffuse uniformly in the chamber space. Initially they tend to accumulate in different horizontal zones according to their relative density compared to the air present in the chamber. Septic tanks are designed to have slow flow rate of sewage, therefore, do not have any significant turbulence in air inside. In the tank described in 1.6, indicate the zones in the air space (A, B, or C as shown below), in which each of the three gases ( $CH_4$ ,  $H_2S$ ,  $CO_2$ ) escaping from the sewage would accumulate initially.



$CH_4$

$CO_2$

$H_2S$

(1.5 marks)

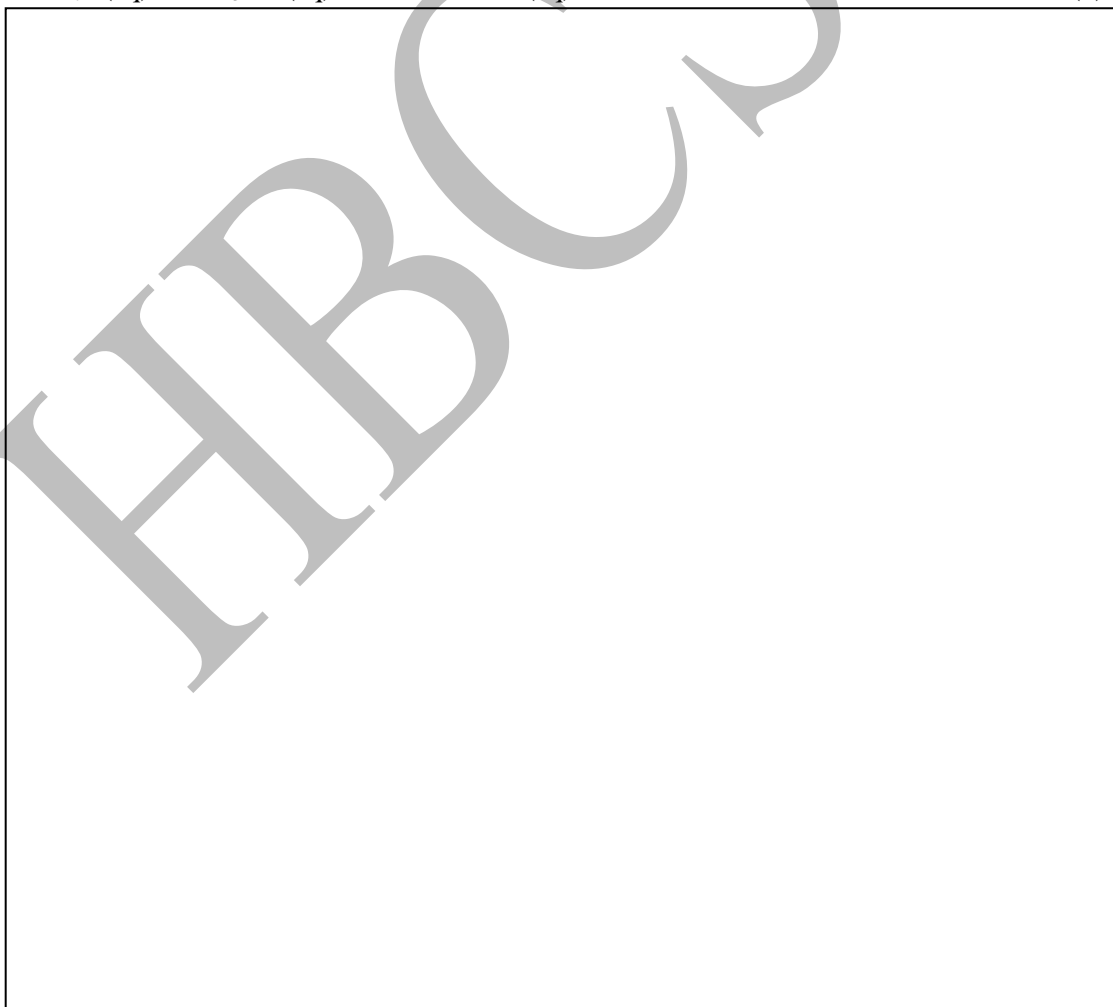
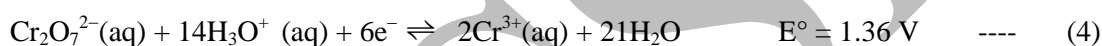
1.8 Water vapour in this air condenses on the tank walls.  $H_2S$  in the air then slowly dissolves in these droplets. Since oxygen is available in immediate vicinity of the droplets (because of high surface area to volume ratio as compared to sewage below), sulphur oxidizing bacteria (SOB) start accumulating in these droplets. In this new aqueous system, SOB oxidize sulphide species and produce sulphuric acid. The cement part in concrete walls can be represented as  $(CaO)_3(Al_2O_3)$ , which is attacked by sulphuric acid. Write the balanced reaction(s) responsible for sulphuric acid production in the water droplets and its possible reaction/s with the cement in concrete.



(1.5 marks)

Wastewater from tanneries contains high amounts of  $\text{SO}_4^{2-}$  and Cr(VI) species. Since Cr(VI) species are highly toxic, such wastewater is often treated with reducing agents such as sucrose to reduce Cr(VI) to Cr(III) before discharging. However, on exposure to air, Cr(III) species may get oxidized back to  $\text{Cr}_2\text{O}_7^{2-}$ .

- 1.9 A tannery wastewater containing  $50 \text{ mg L}^{-1}$  Cr(III) and  $100 \text{ mg L}^{-1}$   $\text{SO}_4^{2-}$  having a  $\text{pH} = 7.0$  is discharged in an open drain exposed to atmosphere. If atmospheric air contains 21.9% oxygen by mass, rest being predominantly nitrogen, calculate the ratio of  $\text{Cr}_2\text{O}_7^{2-}$  to Cr(III) after it has attained equilibrium with the atmospheric air.



(4 marks)

As wastewater flow in open drains, its volume slowly decreases due to evaporation of water. In the open drain described in **1.9**, the water volume reduced by 30% on travelling 1 km.

- 1.10** Determine the equilibrium concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cr(III)}$  and  $\text{Cr}_2\text{O}_7^{2-}$  in the wastewater after this 1 km travel.



**(1.5 marks)**

After this 1 km stretch, the wastewater in **1.10** enters a closed sewer containing sewage, where oxygen is not available. Here, SRB would reduce sulphate to sulphide which can reduce  $\text{Cr}_2\text{O}_7^{2-}$  back to  $\text{Cr(III)}$ .

- 1.11** Write balanced chemical equations for the reactions and their standard electrochemical potentials which would determine the concentrations of  $\text{Cr(III)}$  and  $\text{Cr}_2\text{O}_7^{2-}$  in this sewer, assuming they are solely driven by sulphate-sulphide inter-conversion.



**(2.5 marks)**

Name of Student

Roll No

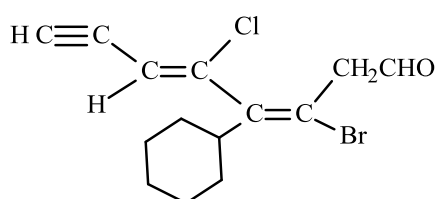
Problem 2

24 Marks

Olefin Chemistry

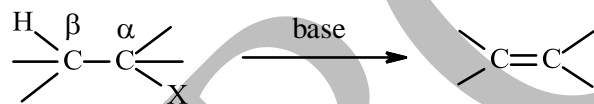
Formation of carbon - carbon double bond (C=C) is important in organic synthesis as it provides a route for introduction of a wide range of functional groups in the resulting olefins. The geometric isomers of olefins are distinguished using stereodescriptors *E/Z*. If the two groups of higher priority, according to the Cahn – Ingold – Prelog rules, are on the opposite sides of the double bond, the configuration is *E*. The other configuration is *Z*.

2.1 Give the IUPAC name with stereochemical descriptor (*E/Z*) for the following compound.



(2 marks)

One of the most widely used methods for the formation of C=C is  $\beta$  - elimination reaction of the following type.

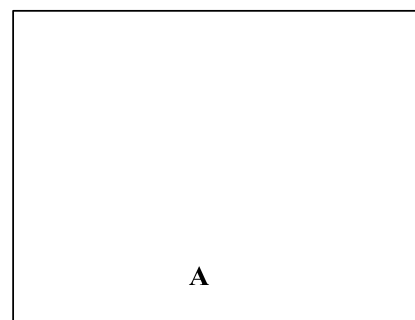
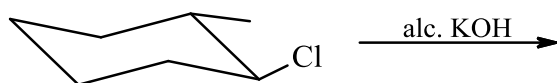


Where X = -Cl, -OCOR,  $-\text{NR}_3^+$  etc.

The spatial arrangement for a bimolecular elimination ( $E_2$ ) of the type shown above requires a *trans* geometry of the  $\beta$  - hydrogen and the leaving group (X). In most of the cases, the most substituted olefin is the favored product. However, in the case of ammonium and sulphonate salts, the least substituted olefin is formed as a major product.

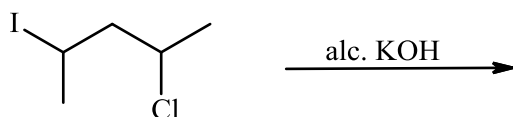
2.2 Identify the major products **A-D** in each of the following reactions, indicating the correct stereochemistry wherever applicable.

i)





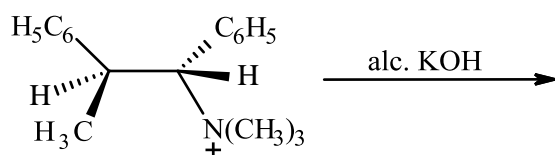
ii)



**B**

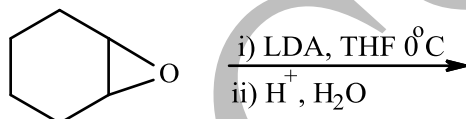
% C = 57.4

iii)



**C**

iv)



**D**

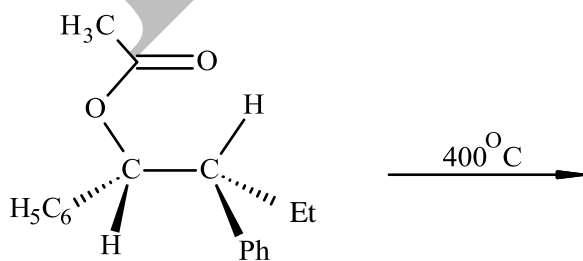
% C = 73.5 %H = 10.2

(2.5 marks)

Pyrolytic elimination is another synthetic route to generate alkenes. This reaction proceeds in a concerted manner through a cyclic transition state. The commonly used substrates in pyrolysis include carboxylate esters, sulfoxides, xanthates, etc. Such reactions proceed in a *syn* fashion, the hydrogen and the leaving group depart from the same side.

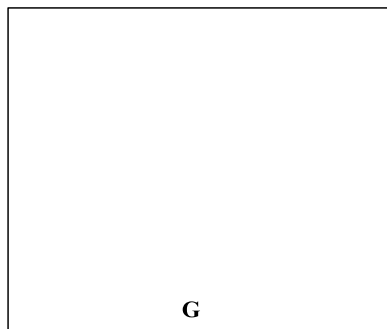
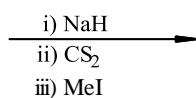
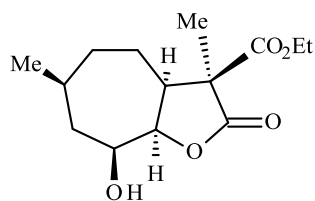
2.3 Identify the products **F-H** in the following reactions indicating the correct stereochemistry wherever applicable.

i)

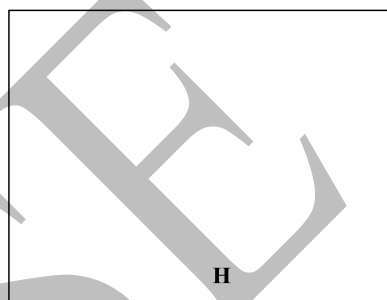


**F**

ii)

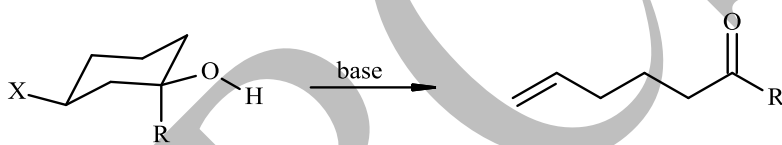


200°C

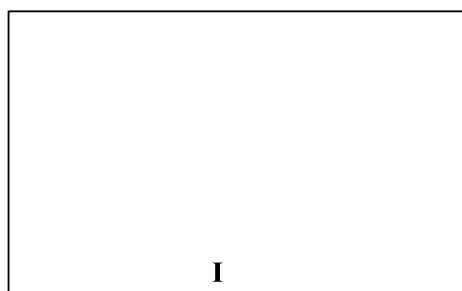
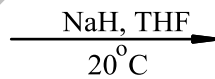
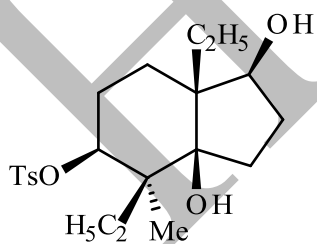


(3 marks)

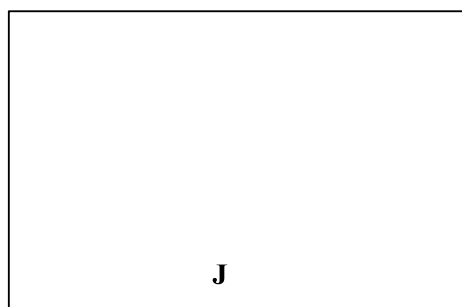
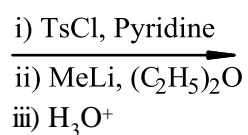
Fragmentation reactions similar to  $\beta$  - elimination are useful for the preparation of olefins. One such reaction is shown below.



- 2.4 Identify the products **I-K** with proper stereochemistry, in the following reaction sequence which leads to an intermediate useful in the synthesis of the juvenile hormone, which regulates insect physiology.



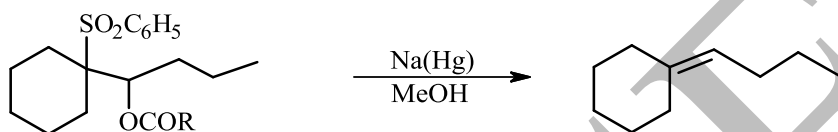
**I**



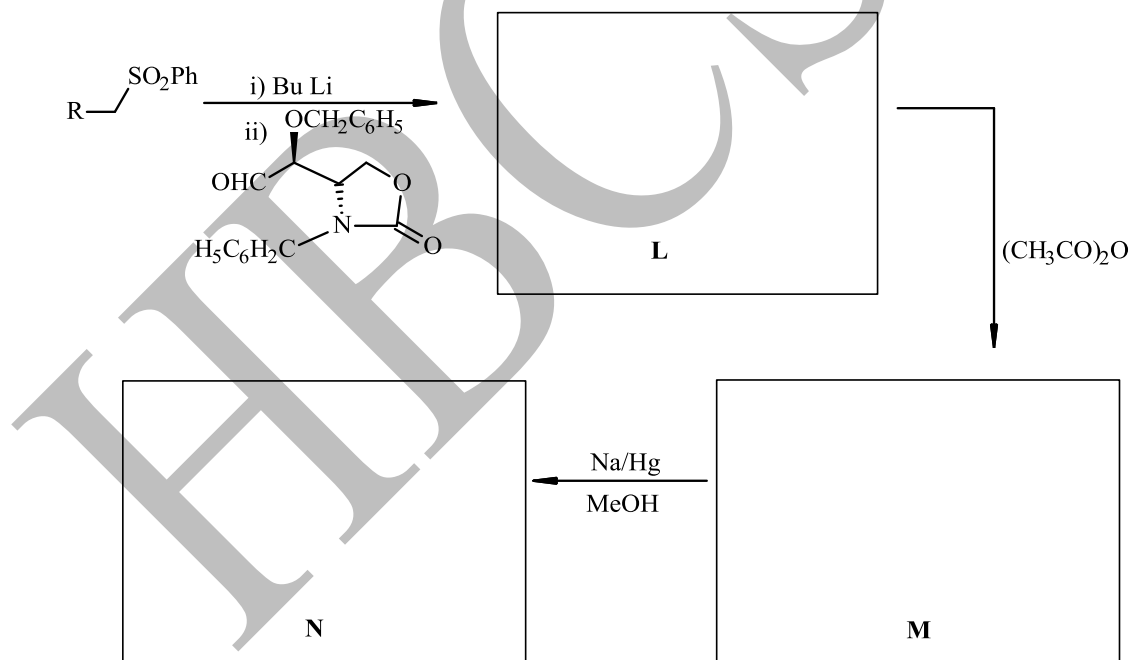


(3.5 marks)

One of the routes for the synthesis of *E*-olefins is the Julia olefination, where the starting compound is a sulfone having a good leaving group at the  $\beta$ -position.

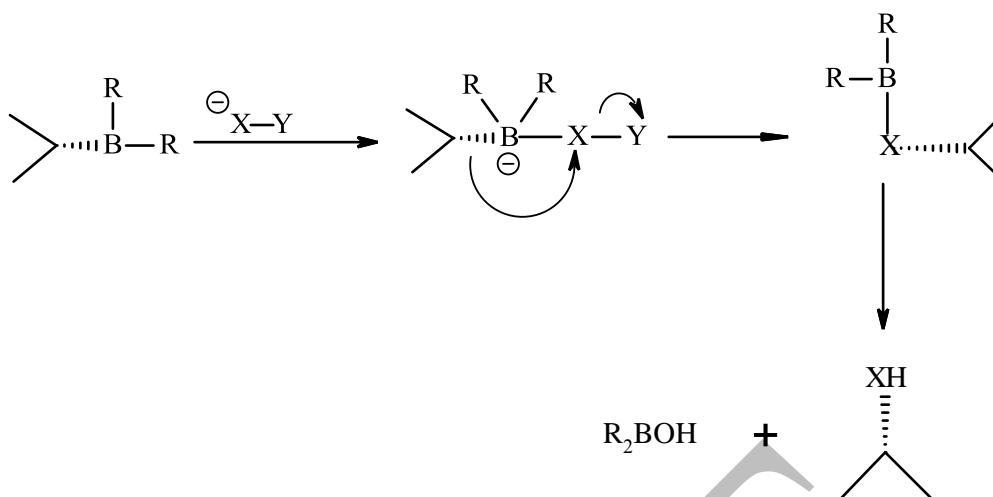


- 2.5 Sphingolipids are naturally occurring compounds which are believed to protect the cell surface from harmful environmental factors. Identify the products **L-N** in the following synthesis which yields the precursor of sphingosins, that forms the backbone of sphingolipids.

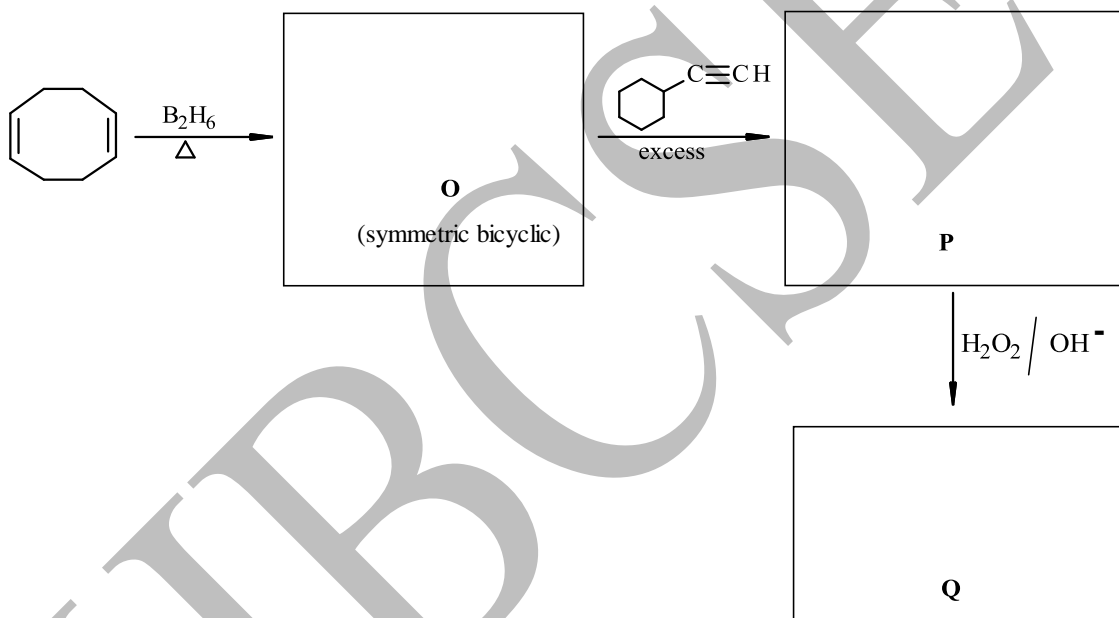


(2.5 marks)

Diboranes add readily to alkenes to give monoalkyl, dialkyl or trialkyl organoborane compounds. Organoboranes can be converted to C-O, C-N and C-C bonds via initial nucleophilic attack followed by rearrangement as illustrated below.

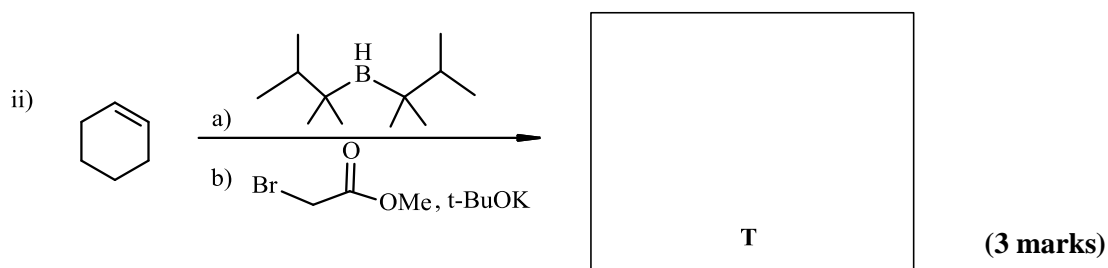
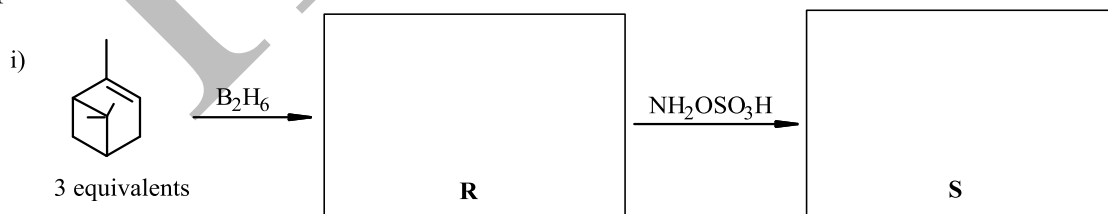


2.6 Complete the following reactions by identifying the compounds **O-Q**.



(3 marks)

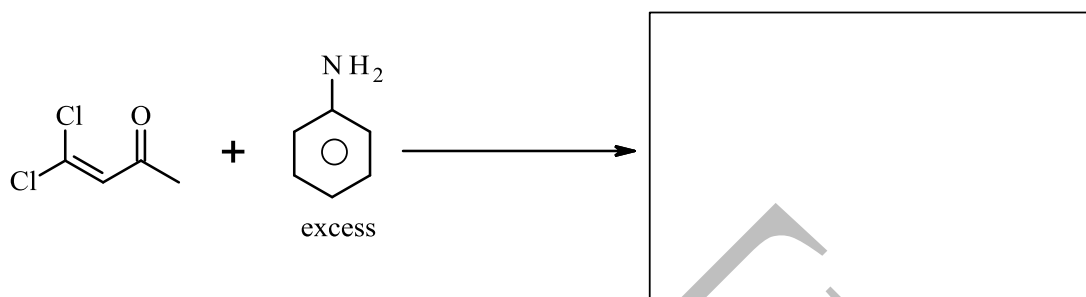
2.7 Give the products **R-T** in the following reactions with correct stereochemistry wherever applicable.



(3 marks)

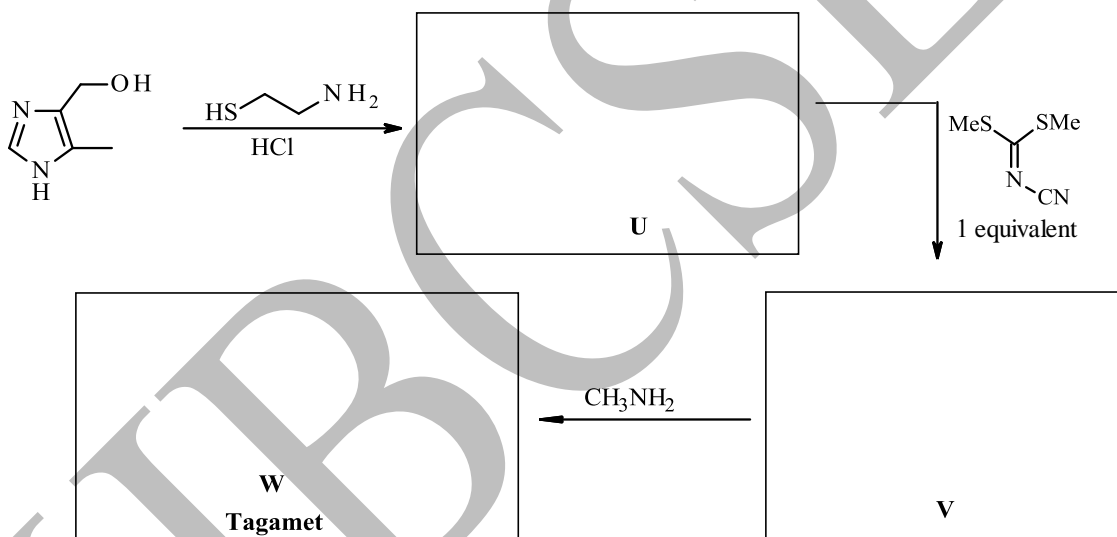
While olefins are nucleophilic, presence of an electron withdrawing group attached to the olefinic carbon renders it electrophilic. Such olefins can undergo conjugate substitution reaction in the presence of good leaving groups at the  $\beta$  - position.

2.8 Give the product of the following reaction.



(1 mark)

2.9 Complete the synthesis of the anti - ulcer drug Tagamet, by identifying U-W.



(3.5 marks)

Name of Student

Roll No

Problem 3

17 marks

Chemical Kinetics and Nuclear Reactions

Part A

The reaction between  $\text{BrO}_3^-$  and  $\text{Br}^-$  in acidic solution results in the formation of  $\text{Br}_2$  and  $\text{H}_2\text{O}$  and the rate law is given by,

$$r = -\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

3.1 Write the stoichiometric equation corresponding to this reaction.

(1 mark)

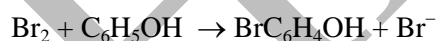
3.2 Write the total order of the reaction.

(1 mark)

3.3 Simplify the rate law for the same reaction if  $[\text{BrO}_3^-]_0 = 2.5 \times 10^{-3} \text{ M}$ ,  $[\text{H}^+]_0 = 1.0 \text{ M}$  and  $[\text{Br}^-]_0 = 0.28 \text{ M}$  where the subscript zero refers to initial concentration.

(1 mark)

To study the kinetics of the above reaction, a student added phenol to the above reaction mixture, which undergoes the following reaction:



To detect the completion of the above monobromination reaction, the student added a drop of dilute methyl orange solution to the reaction flask. Methyl orange gets bleached by  $\text{Br}_2$  and becomes colourless immediately even at very low  $\text{Br}_2$  concentrations.

Monobromination of phenol, ( $\text{C}_6\text{H}_5\text{OH}$ ) is a much faster reaction than the bromate-bromide reaction. The student prepared three reaction flasks as given in the table below. The student measured the time,  $t$ , it takes for the solution at different concentrations of phenol to turn colourless.

Flask No.	[C <sub>6</sub> H <sub>5</sub> OH] (M)	[Br <sup>-</sup> ] (M)	[H <sup>+</sup> ] (M)	[BrO <sub>3</sub> <sup>-</sup> ]* (M)	Time taken for decolourization, <i>t</i> (sec)
1	4 × 10 <sup>-3</sup>	0.28	1.0	2.5 × 10 <sup>-3</sup>	11
2	2 × 10 <sup>-3</sup>	0.28	1.0	2.5 × 10 <sup>-3</sup>	4
3	1 × 10 <sup>-3</sup>	0.28	1.0	2.5 × 10 <sup>-3</sup>	1.5

\*BrO<sub>3</sub><sup>-</sup> is added in the last just before starting the experimental run.

**3.4** On doubling the concentration of C<sub>6</sub>H<sub>5</sub>OH, (in the above table) *t* increased by more than a factor of two because (put X against the correct option/s)

- i) the decolouration reaction of methyl orange slowed down at higher concentration of phenol
- ii) the bromination of phenol slowed down at higher concentration of phenol
- iii) at higher concentration of phenol, BrC<sub>6</sub>H<sub>4</sub>OH started converting to Br<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH
- iv) the rate of bromate-bromide reaction decreases with progress of reaction overtime.
- v) at higher concentration of phenol, the simplified rate law derived in 3.3 is no longer valid

(2 marks)

**3.5** Calculate the rate constant, *k*, of bromate-bromide reaction using the data given in the above table. Show all important steps in the calculations.

(3 marks)

3.6 Another way to do this experiment is to keep the phenol concentration fixed and vary  $[\text{BrO}_3^-]_0$ . In such an experiment, (mark **X** against the correct option/s)

- (i)  $t$  will increase as  $[\text{BrO}_3^-]_0$  increases
- (ii)  $k$  can be obtained from the initial slope of  $[\text{BrO}_3^-]$  vs  $t$  plot fit to an exponential curve
- (iii) the experiment become less accurate as  $[\text{BrO}_3^-]_0/[\text{C}_6\text{H}_5\text{OH}]_0$  decreases
- (iv)  $t$  will be independent of  $[\text{Br}^-]_0$
- (v)  $k$  can be obtained using the slope of  $1/t$  vs  $[\text{BrO}_3^-]$  plot fit to a line

(2 marks)

**Part B**

3.7 Radioactive  $^{238}\text{U}_{92}$  emits alpha and beta particles and forms stable  $^{206}\text{Pb}_{82}$ .

i) Write the balanced overall nuclear reaction.

(1 mark)

ii) An uranium ore sample is found to contain 1.19 g of  $^{238}\text{U}_{92}$  and 1.03 g of  $^{206}\text{Pb}_{82}$ . (Assume that there was no lead initially in the ore).

a) What mass of helium has escaped from the ore sample?

(1 mark)

b) How old is the ore? Half of  $^{238}\text{U}_{92}$  converts to  $^{206}\text{Pb}_{82}$  in 1.0 billion years.

(1 mark)

3.8  $^{239}\text{U}_{92}$  decays to  $^{239}\text{Pu}$  through the formation of an intermediate nucleus  $^{239}\text{Np}$ , the successive decay constants being  $k_1$  and  $k_2$ .

i) Write the rate equation for decay of both  $^{239}\text{U}$  and  $^{239}\text{Np}$ .

(1.5 marks)



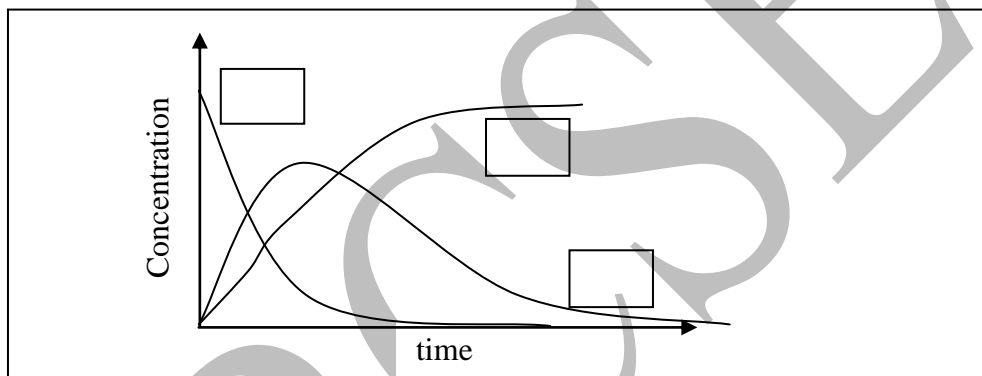
The concentration of  $^{239}\text{Np}$  can be expressed by the following expression.

$$[^{239}\text{Np}] = \frac{k_1 [^{239}\text{U}]}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

ii) Simplify the expression using suitable approximation if the half lives for the decay of the two nuclei are 23.5 minutes and 2.35 days, respectively.

(1mark)

iii) Following graph shows the concentration profiles for U, Np and Pu as a function of time. Label each curve with the corresponding species.



(1mark)

iv) State whether the following statement is true or false.

Nuclear disintegration rate approximately doubles for every  $10^\circ\text{C}$  rise in temperature.

(Mark X the appropriate choice).

True

False

(0.5 mark)

Name of Student

Roll No

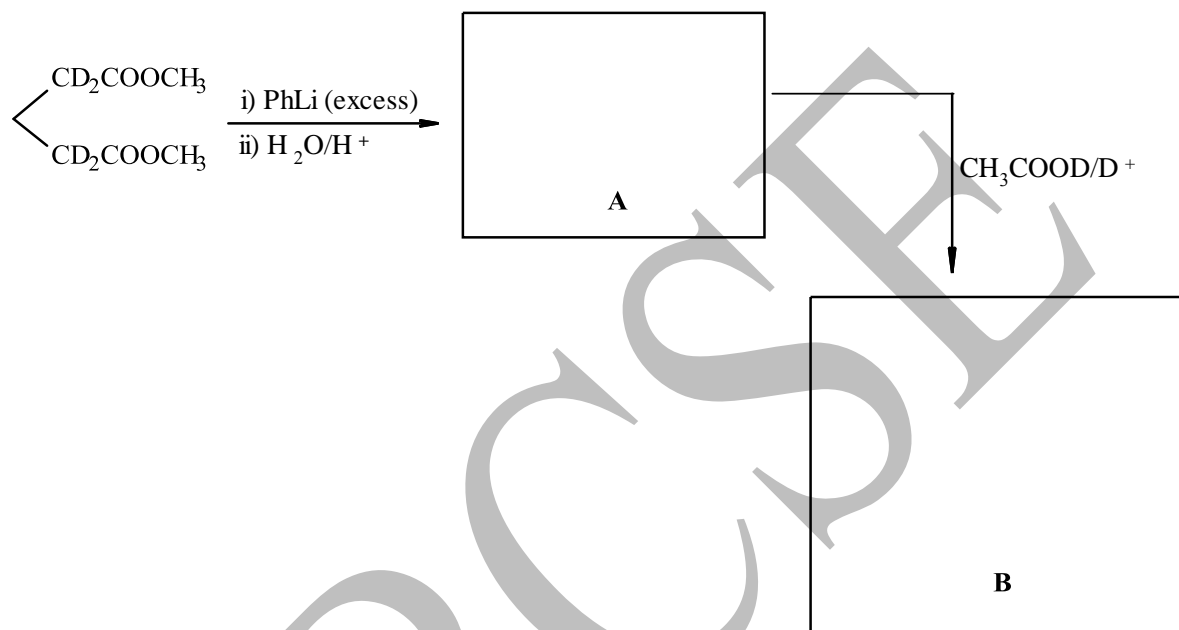
Problem 4

17 Marks

Synthesis of Natural Products

Nonconjugated dienes are important intermediates in natural product synthesis. One of the simple ways to synthesize these compounds is outlined below.

4.1 Identify products **A** and **B** in the following synthesis of a 1,4 diene.

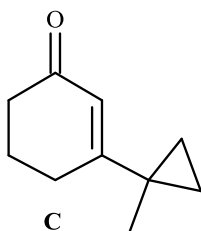


(1.5 marks)

Di-pi methane rearrangement is an important photochemical reaction in which nonconjugated dienes form an ene-substituted cyclopropane, as shown below.



Zizaene is a naturally occurring terpene found in vetiver oil and used for the synthesis of  $\alpha$ -vetivone that is used in perfumeries. It is prepared from compound **C**.

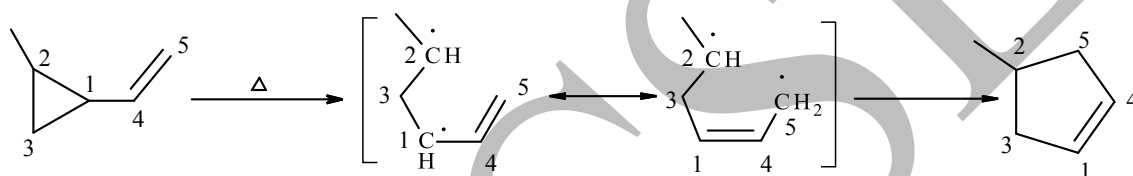


- 4.2 Draw the structure of the precursor of **C**, if it was to be prepared by the di-pi methane rearrangement.



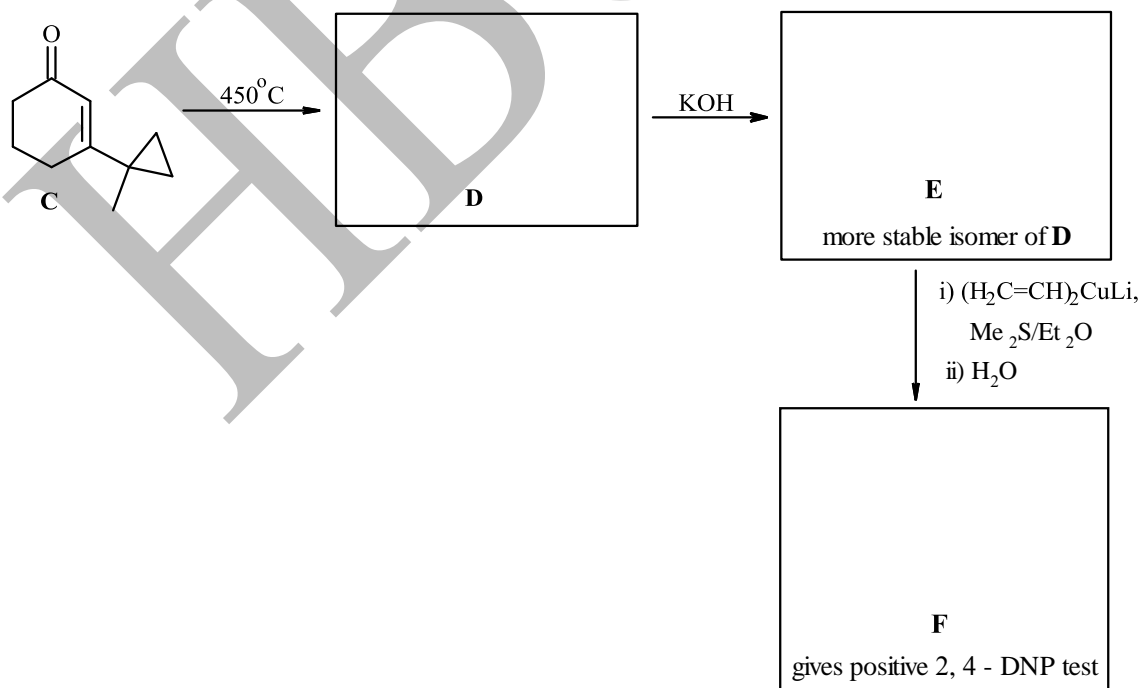
(1 mark)

Vinyl cyclopropane to cyclopentene rearrangement (shown below) is an important method for the synthesis of five membered carbocycles. This rearrangement can be performed under thermal, photochemical or catalytic activation. Under thermal and photochemical conditions, this rearrangement proceeds via formation of the most stable biradical.



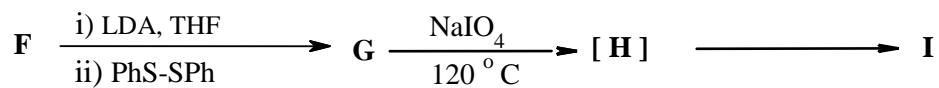
The vinyl cyclopropane rearrangement is a key step in the synthesis of Zizaene. The synthesis of Zizaene is outlined below.

- 4.3 Draw the structures of **D** – **F** in the following reaction sequence.



(2.5 marks)

Compound **F** on reaction with  $\text{LiN}(\text{i-Pr})_2$  (**LDA**) (LDA is a bulky base) and PhS-SPh gives compound **G**, which on further oxidation using  $\text{NaIO}_4$  gives intermediate **H** and product **I**.

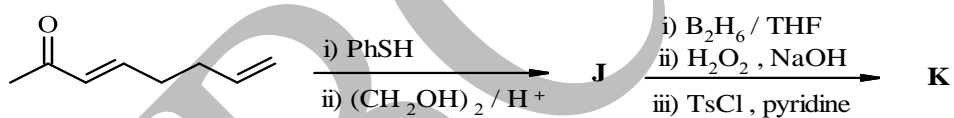


4.4 Identify **G**, **H** and **I**.

<b>G</b>	<b>H</b> Intermediate	<b>I</b> % C = 81.77 % H = 9.15
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(2 marks)

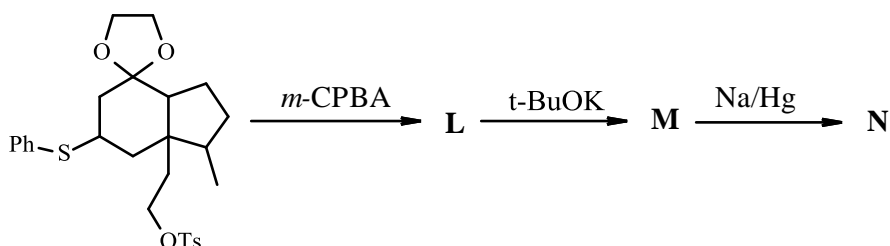
4.5 Draw the structures of **J** and **K** in the following reaction.



<b>J</b>	<b>K</b>
----------	----------

(3 marks)

Compound **N** is an intermediate for the synthesis of Zizaene. It is synthesized as shown below.

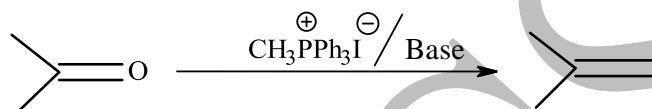


4.6 Identify L, M and N.

<p><b>L</b></p> <p>%C = 60.55 %H = 6.41 %O = 20.95</p>	<p><b>M</b></p>	<p><b>N</b></p> <p>%C = 75.63 %H = 9.97</p>
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(3.5 marks)

Ylide is a species with a positive charge on a hetero atom and a negative charge on the adjacent carbon atom. Wittig reaction is a reaction which involves the phosphorous ylide.



4.7 Identify O and P. Draw the structure of Zizaene.



<p><b>O</b></p>	<p><b>P</b></p>	<p><b>Zizaene</b></p>
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(3 marks)

4.8 How many stereocenters does Zizaene have?

(0.5 marks)

Name of Student

Roll No

**Problem 5**

**24 Marks**

**Nickel and its chemistry**

Commercially important nickel ores include its sulfide, which also contains iron (II) and copper (I) sulfides. The concentrated ore is smelted in presence of silica which helps in removal of iron as slag (Step I). The upper silvery layer of  $\text{Cu}_2\text{S}$  and lower black layer of  $\text{Ni}_2\text{S}_3$  remaining with the ore are then mechanically separated. The  $\text{Ni}_2\text{S}_3$  is roasted in air to give a green solid (Step-II), which on subsequent treatment with water gas (mixture of CO and  $\text{H}_2$  gas) at  $50^\circ\text{C}$  gives a volatile complex and other byproducts (Step-III). This complex on thermal decomposition in air at  $230^\circ\text{C}$  gives pure solid Ni (Step-IV).

**5.1** i) Write the balanced chemical equations for Steps I – IV.

Step I:	
Step II:	
Step III:	
Step IV:	

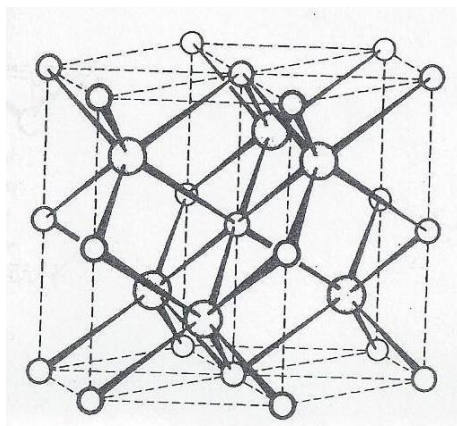
**(2.5 marks)**

ii) Which of the following statements is / are true for Step III (Mark **X** in the correct box/es):

- |  |                          |
|--|--------------------------|
| a) Only $\text{H}_2$ from water gas reacts with Ni ions and reduces it                           | <input type="checkbox"/> |
| b) $\text{H}_2$ from water gas reduces Ni ions and then CO complexes with the reduced form of Ni | <input type="checkbox"/> |
| c) Only CO from water gas reduces Ni ions  | <input type="checkbox"/> |
| d) Both CO and $\text{H}_2$ from water gas act as reducing agents                                | <input type="checkbox"/> |

**(1mark)**

Pure nickel forms alloys with various metals such as As, Al, Cd, Cr, Zn etc. and some of these have well defined crystal structure. The unit cell of  $Ni_xAs_y$  is shown in the following figure.



○ As  
○ Ni

Diagram sourced from *Structural Inorganic Chemistry*, A F Wells, 5<sup>th</sup> Reprint edition, 2012, Oxford University Press, Oxford.

- 5.2 i) Using the above diagram identify the coordination number and geometries of Ni and As. (Mark X in the correct box)

Element	Coordination No.		Coordination geometry			
	6	4	Octahedral	Trigonal Prismatic	Square planar	Tetrahedral
Ni	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
As	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

(2 marks)

- ii) Find the values of x and y in  $Ni_xAs_y$ .

x =	y =
-----	-----

(0.5 mark)

Nickel forms various alloys such as stainless steel, nichrome and cupranickel which have various applications in industries.

Stainless steel has the following approximate composition (w/w): 73% Fe, 18% Cr and 8% Ni. An industrial sample of stainless steel was analyzed for its nickel content using chemical methods. One of the standard quantitative methods for estimation of nickel utilizes two moles of

chelating bidentate ligand, dimethylglyoxime [DMG,  $\text{CH}_3\text{C}(\text{NOH})\text{C}(\text{NOH})\text{CH}_3$ ]. Nickel precipitates as a neutral complex ( $\text{C}_8\text{H}_{14}\text{O}_4\text{N}_4\text{Ni}$ ), dark pink in color.

- 5.3 i) Draw the structure of the complex formed.

(1 mark)

1.4 g of stainless steel sample was treated with aqua-regia to dissolve all the contents of the sample. The solution was treated for removal of iron and chromium ions and was then diluted to 100 mL using distilled water. 10 mL of this diluted solution when treated with DMG gave 0.0532 g of the precipitate of the complex.

- ii) Calculate the % of nickel in the sample taken for analysis. Show all important steps of calculations.

(2 marks)

The stability of nickel complexes can be understood from their formation constant,  $K$ . The formation constants of the following Ni complexes **X** and **Y** at 25 °C are



- 5.4 i) Draw the structure/s of all possible isomers of **Y** and **encircle** the optically active isomer/s if any.



(2 marks)

- ii) Calculate the entropy change during the formation of **Y** in Equation II at 25 °C, if the heat of reaction for Equation II at constant pressure is  $-12.1 \text{ kJ mol}^{-1}$ .

(2 marks)

Raney nickel is a versatile hydrogenation catalyst. It is prepared by leaching out Al selectively from Ni-Al alloy powder under controlled condition by treating with concentrated solution of caustic soda. The slurry of finely divided spongy nickel particles is thus obtained which is then washed with large quantities of water to make the particles free from caustic soda.

- 5.5 Write balanced chemical equation for leaching process during the preparation of catalyst.

(1 mark)

Green nickel oxide NiO can be doped with colorless lithium oxide,  $\text{Li}_2\text{O}$ , to give a black solid  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  which acts as a semiconductor.

- 5.6 Which of the following statement(s) is/are correct for the above observations? (Mark **X** in the correct box)

- i)  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  exhibits both cationic and anionic vacancies
- ii)  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  exhibits Schottky defect
- iii) Doping of NiO with lithium induces mixed valency of nickel
- iv) NiO becomes a p-type semiconductor


(1mark)

Mixed metal oxides of transition metals often form spinels having the general formula  $A^{II}B^{III}_2O_4$  where the oxide ions form a close packed cubic lattice with eight tetrahedral holes and four octahedral holes per  $A^{II}B^{III}_2O_4$  unit. In a normal spinel  $1/8^{\text{th}}$  of the tetrahedral holes are occupied by A (II) whereas B (III) resides in octahedral sites. In inverse spinel A (II) and one half of B (III) occupy the octahedral holes while the other half of B (III) occupy the tetrahedral holes. The structure becomes ‘normal’ ( $A^{II}B^{III}_2O_4$ ) or ‘inverse’ spinel ( $B^{III}A^{II}B^{III}O_4$ ) depending upon the octahedral site preference energy which is the difference of the crystal field stabilization energy (CFSE) of the same cation in the corresponding octahedral and tetrahedral field of the ligand.

Metal ion	$\Delta_0$ (cm <sup>-1</sup> )	$\Delta_t$ (cm <sup>-1</sup> )
Co <sup>3+</sup>	20,760	9,226
Fe <sup>3+</sup>	14,000	6,220
Ni <sup>2+</sup>	8,500	3,780

( $\Delta_0$  and  $\Delta_t$  imply the octahedral and tetrahedral splitting parameters respectively for oxide ions which will provide a moderately weak field similar to that of water)

5.7 On the basis of the above data, calculate the CFSE for

- Case I:            i) Co(III) in octahedral                      ii) Co(III) in tetrahedral sites  
 Case II:            i) Fe (III) in octahedral                      ii) Fe(III) in tetrahedral sites  
 Case III:            i) Ni(II) in octahedral                      ii) Ni(II) in tetrahedral sites

**(Calculations involving pairing energies can be neglected for this question and only CFSE values can be calculated)**

Case I

Case II

Case III

(2.5 marks)

iii) Calculate the octahedral site preference energy from 5.7 for all the above three cases.

Case I
Case II
Case III

(1 mark)

iv) Based on the above octahedral site preference energy calculations, classify the oxides as normal and inverse spinels. (Mark X in the correct box)

Compound	Normal	Inverse
NiFe <sub>2</sub> O <sub>4</sub>		
NiCo <sub>2</sub> O <sub>4</sub>		

(1 mark)

5.8 One of the widely used batteries of nickel is Ni-Cd battery. This battery uses high purity NiOOH (nickel oxyhydroxide) as anode. The typical synthesis of NiOOH is as follows.

In the first step, concentrated NaOH (30% w/v) is reacted with gaseous Cl<sub>2</sub> for sufficient time to generate hypochlorite.

i) Write balanced chemical equation for this reaction.

(0.5 mark)

The resultant reaction mixture is then treated with excess of solid NaOH with vigorous stirring which leads to precipitation of NaCl. The precipitate is filtered and the sufficient amount of Ni(OH)<sub>2</sub> is added to the filtrate with constant stirring. Black colored NiOOH is formed as suspension.

ii) Write the balanced chemical equation that leads to formation of NiOOH.

(1 mark)

The NiOOH suspension thus obtained is filtered and dried appropriately. However, before its use, it needs to be analyzed for its purity.

In one such analysis, 0.520 g of NiOOH sample prepared by the above method was treated with 25 mL of acidified 0.305 M Fe (II) solution. On dissolution, Fe(II) ions get oxidized quantitatively by Ni ions. The unreacted Fe(II) was titrated with 0.0285 M of  $\text{KMnO}_4$  under acidic condition and the observed reading was 15.1 mL.

**5.9** Write balanced chemical equations for-

- i) Reaction of NiOOH with acidified Fe(II)
- ii) Reaction involved in titration with  $\text{KMnO}_4$

i)
ii)

**(1 mark)**

- iii) Calculate the percentage of NiOOH in the sample taken for analysis. Show the main steps of calculations.

--

**(2 marks)**

# Periodic Table of the Elements

1 IA 11A <b>H</b> Hydrogen 1.008																	2 IIA 2A <b>He</b> Helium 4.003
3 <b>Li</b> Lithium 6.941	4 <b>Be</b> Beryllium 9.012											5 <b>B</b> Boron 10.811	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998	10 <b>Ne</b> Neon 20.180
11 <b>Na</b> Sodium 22.990	12 <b>Mg</b> Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 <b>Al</b> Aluminum 26.982	14 <b>Si</b> Silicon 28.086	15 <b>P</b> Phosphorus 30.974	16 <b>S</b> Sulfur 32.066	17 <b>Cl</b> Chlorine 35.453	18 <b>Ar</b> Argon 39.948
19 <b>K</b> Potassium 39.098	20 <b>Ca</b> Calcium 40.078	21 <b>Sc</b> Scandium 44.956	22 <b>Ti</b> Titanium 47.88	23 <b>V</b> Vanadium 50.942	24 <b>Cr</b> Chromium 51.996	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Iron 55.933	27 <b>Co</b> Cobalt 58.933	28 <b>Ni</b> Nickel 58.693	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.39	31 <b>Ga</b> Gallium 69.732	32 <b>Ge</b> Germanium 72.61	33 <b>As</b> Arsenic 74.922	34 <b>Se</b> Selenium 78.09	35 <b>Br</b> Bromine 79.904	36 <b>Kr</b> Krypton 84.80
37 <b>Rb</b> Rubidium 84.468	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.906	40 <b>Zr</b> Zirconium 91.224	41 <b>Nb</b> Niobium 92.906	42 <b>Mo</b> Molybdenum 95.94	43 <b>Tc</b> Technetium 98.907	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.906	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.868	48 <b>Cd</b> Cadmium 112.411	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.71	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.6	53 <b>I</b> Iodine 126.904	54 <b>Xe</b> Xenon 131.29
55 <b>Cs</b> Cesium 132.905	56 <b>Ba</b> Barium 137.327	57-71	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.948	74 <b>W</b> Tungsten 183.85	75 <b>Re</b> Rhenium 186.207	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.22	78 <b>Pt</b> Platinum 195.08	79 <b>Au</b> Gold 196.967	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.383	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.980	84 <b>Po</b> Polonium [208.982]	85 <b>At</b> Astatine 209.987	86 <b>Rn</b> Radon 222.018
87 <b>Fr</b> Francium 223.020	88 <b>Ra</b> Radium 226.025	89-103	104 <b>Rf</b> Rutherfordium [261]	105 <b>Db</b> Dubnium [262]	106 <b>Sg</b> Seaborgium [266]	107 <b>Bh</b> Bohrium [264]	108 <b>Hs</b> Hassium [269]	109 <b>Mt</b> Meitnerium [268]	110 <b>Ds</b> Darmstadtium [269]	111 <b>Rg</b> Roentgenium [272]	112 <b>Cn</b> Copernicium [277]	113 <b>Uut</b> Ununtrium unknown	114 <b>Fl</b> Flerovium [289]	115 <b>Uup</b> Ununpentium unknown	116 <b>Lv</b> Livermorium [298]	117 <b>Uus</b> Ununseptium unknown	118 <b>Uuo</b> Ununoctium unknown

Lanthanide Series	57 <b>La</b> Lanthanum 138.906	58 <b>Ce</b> Cerium 140.115	59 <b>Pr</b> Praseodymium 140.908	60 <b>Nd</b> Neodymium 144.24	61 <b>Pm</b> Promethium 144.913	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.966	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.925	66 <b>Dy</b> Dysprosium 162.50	67 <b>Ho</b> Holmium 164.930	68 <b>Er</b> Erbium 167.26	69 <b>Tm</b> Thulium 168.934	70 <b>Yb</b> Ytterbium 173.04	71 <b>Lu</b> Lutetium 174.967
Actinide Series	89 <b>Ac</b> Actinium 227.028	90 <b>Th</b> Thorium 232.038	91 <b>Pa</b> Protactinium 231.036	92 <b>U</b> Uranium 238.029	93 <b>Np</b> Neptunium 237.048	94 <b>Pu</b> Plutonium 244.064	95 <b>Am</b> Americium 243.061	96 <b>Cm</b> Curium 247.070	97 <b>Bk</b> Berkelium 247.070	98 <b>Cf</b> Californium 251.080	99 <b>Es</b> Einsteinium [254]	100 <b>Fm</b> Fermium 257.095	101 <b>Md</b> Mendelevium 258.1	102 <b>No</b> Nobelium 259.101	103 <b>Lr</b> Lawrencium [262]