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:

a) **Fill out the top half of the Performance card. Make sure that the performance card is attached to the question paper.**

b) **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 2nd 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 $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$

                              $= 8.314 \text{ K Pa.dm}^3 \text{ K}^{-1}\text{mol}^{-1}$

                              $= 0.082 \text{ L.atm K}^{-1}\text{mol}^{-1}$

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

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

1 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 $m_e = 9.109 \times 10^{-31} \text{ kg}$

Plancks 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 $0°C = 273.15 \text{ K}$

Name of Student	Roll No

**Problem 1**   **20 Marks**
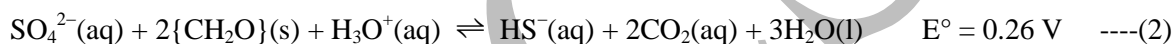
Sulphate dynamics in Wastewaters

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:

$$SO_4^{2-}\,(aq) + 9H_3O^+(aq) + 8e^- \;\rightleftharpoons\; HS^-(aq) + 13H_2O \qquad\qquad E^\circ = -\,0.22\ \text{V} \quad \text{----(1)}$$
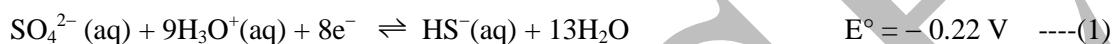
HS^- thus produced gets converted into H_2S.

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

$$SO_4^{2-}(aq) + 2\{CH_2O\}(s) + H_3O^+(aq) \;\rightleftharpoons\; HS^-(aq) + 2CO_2(aq) + 3H_2O(l) \qquad E^\circ = 0.26\ \text{V} \quad \text{----(2)}$$

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, ΔG°, 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 $[SO_4^{2-}] = 0.5$ mM and pH = 7.0. Assuming (2) to be the predominant redox reaction in the sewage, determine the concentration of dissolved H_2S in it when the system reaches equilibrium. (For H_2S, $pKa_1 = 7.0$ and $pKa_2 = 11.96$).

Assume that

(a) H_2S and CO_2 gases produced remain in the solution phase.

(b) the carbonic acid produced here doesn't undergo dissociation.

(c) the sewage acts as buffer.

(2 marks)

Under aerobic conditions, CH_4 is also often produced in the decomposition of sewage in addition to H_2S and 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.
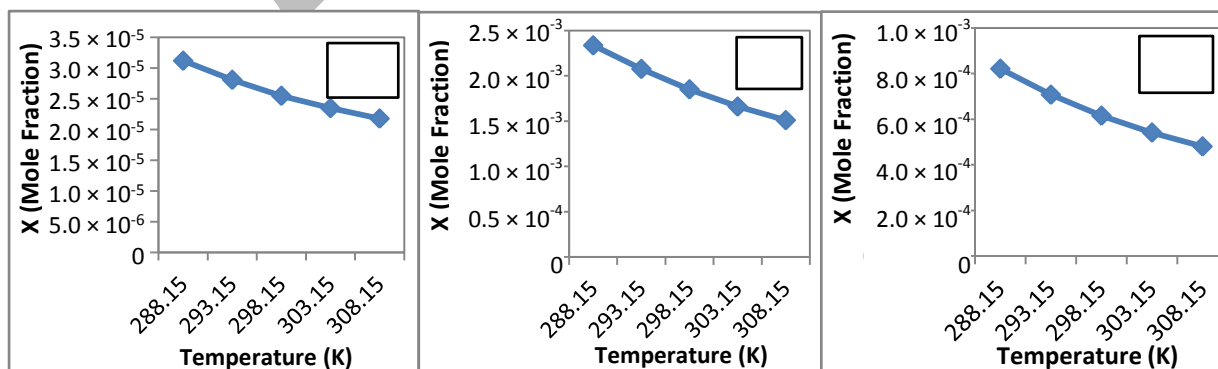
ii) Which of the three gases will escape from sewage the fastest?

(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.
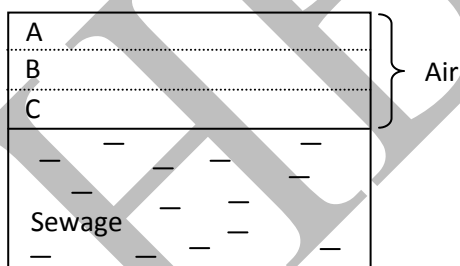
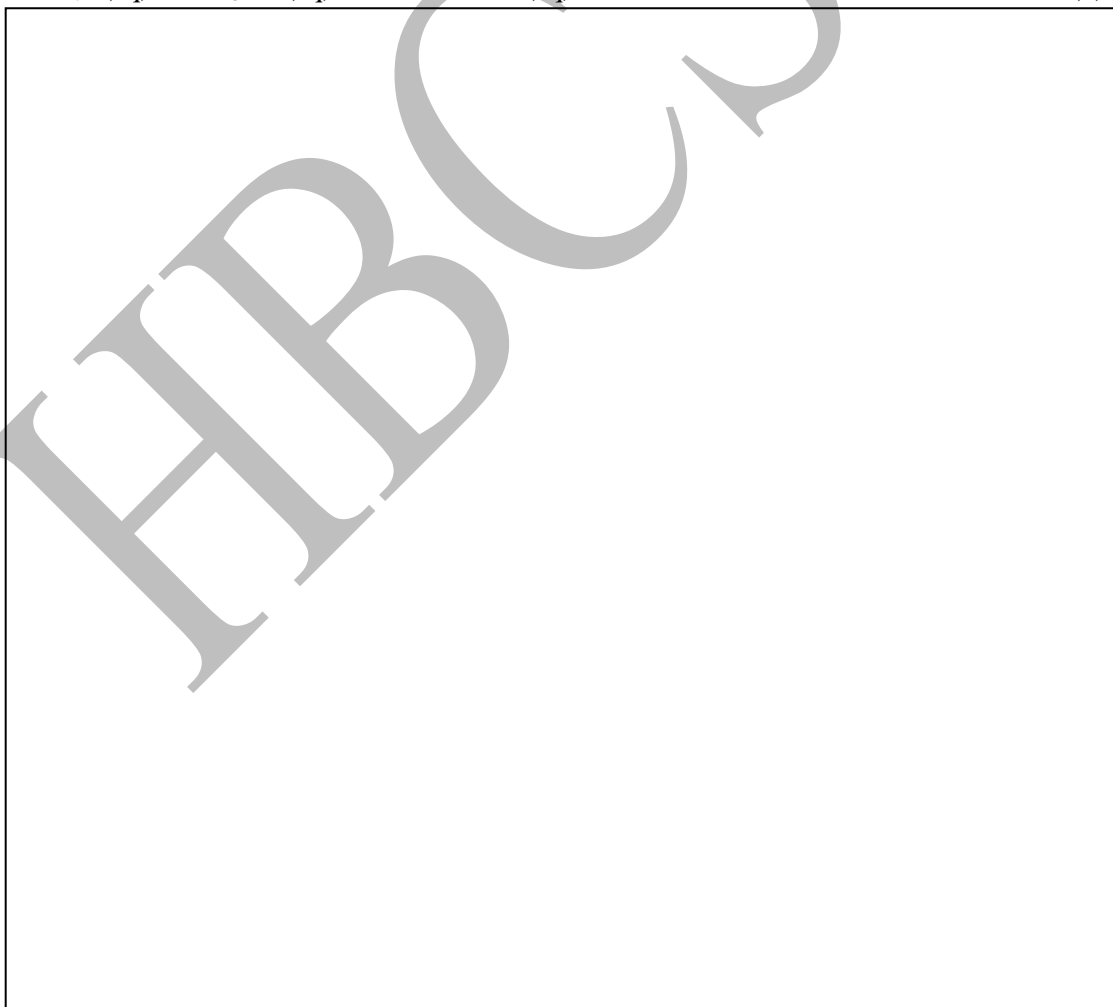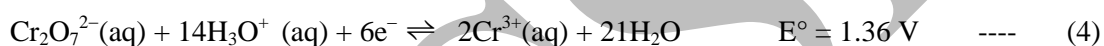CH$_4$ [ ]   CO$_2$ [ ]   H$_2$S [ ]

(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 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 $Cr_2O_7^{2-}$.

1.9   A tannery wastewater containing 50 mg L^{-1} Cr(III) and 100 mg L^{-1} SO_4^{2-} having a 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 $Cr_2O_7^{2-}$ to Cr(III) after it has attained equilibrium with the atmospheric air.

$$O_2 \text{ (g)} + 4H_3O^+ \text{ (aq.)} + 4e^- \rightleftharpoons 6\,H_2O \qquad\qquad E° = 1.23 \text{ V} \quad ---- \quad (3)$$

$$Cr_2O_7^{2-}\text{(aq)} + 14H_3O^+ \text{ (aq)} + 6e^- \rightleftharpoons 2Cr^{3+}\text{(aq)} + 21H_2O \qquad E° = 1.36 \text{ V} \quad ---- \quad (4)$$

(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 SO_4^{2-}, Cr(III) and $Cr_2O_7^{2-}$ 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 $Cr_2O_7^{2-}$ back to Cr(III).

1.11 Write balanced chemical equations for the reactions and their standard electrochemical potentials which would determine the concentrations of Cr(III) and $Cr_2O_7^{2-}$ 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.
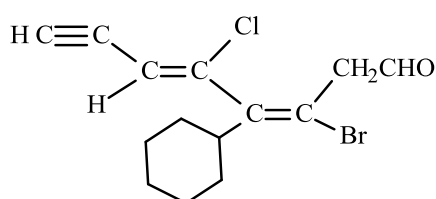
(2 marks)

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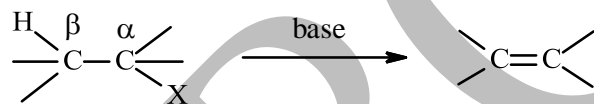

Where X= -Cl, -OCOR, -$^+NR_3$ etc.

The spatial arrangement for a bimolecular elimination (E_2) of the type shown above requires a *trans* geometry of the β - 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.
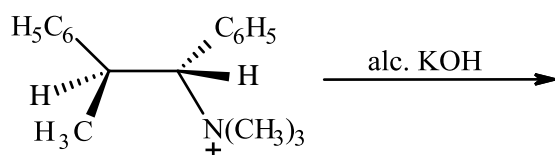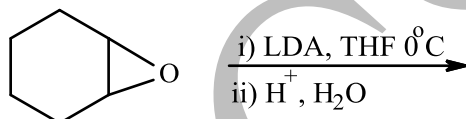
i)

ii)

alc. KOH →

B

% C = 57.4

iii)

alc. KOH →

C

iv)

i) LDA, THF 0°C
ii) H⁺, H₂O →
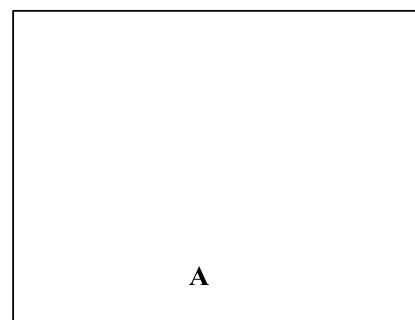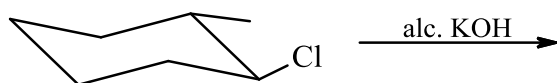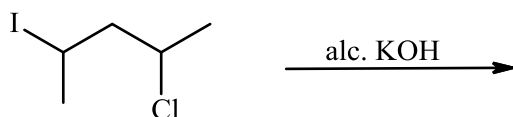
D

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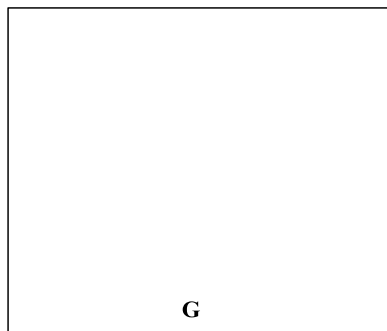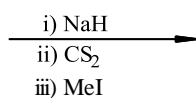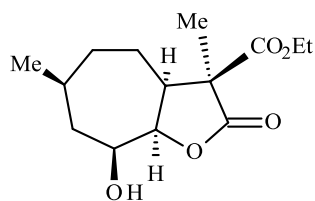
2.3   Identify the products **F-H** in the following reactions indicating the correct stereochemistry wherever applicable.

i)

400°C →

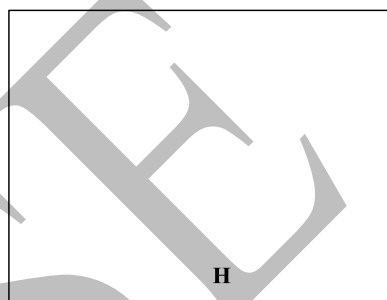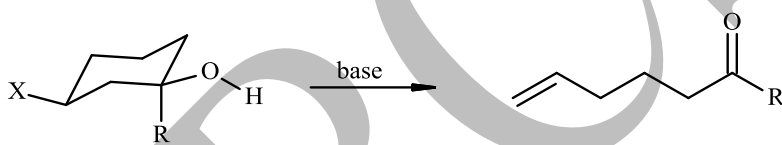**F**

ii)

i) NaH
ii) CS$_2$
iii) MeI

G

200°C

H
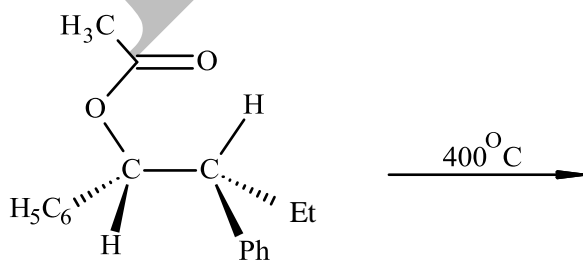
(3 marks)

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

base

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.

NaH, THF
20°C

I

I

i) TsCl, Pyridine
ii) MeLi, (C$_2$H$_5$)$_2$O
iii) H$_3$O$^+$

J

J $\xrightarrow{\text{NaH, THF}}$ K
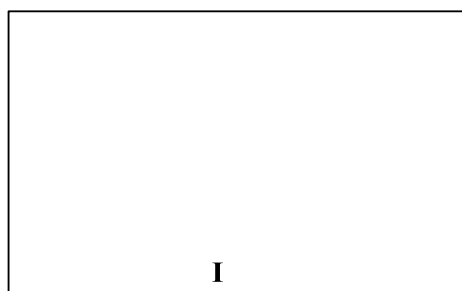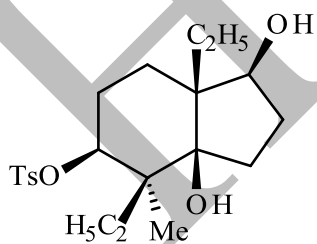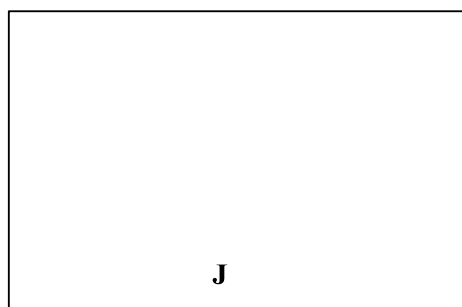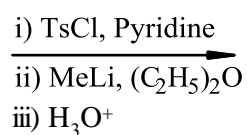
(3.5 marks)

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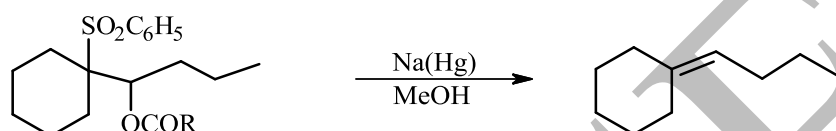
2.5 Sphingolipids are naturally occurring compounds which are believed to protect the cell surface from harmful environmental factors. Identify the products **L-N** in the following synthesis which yields the precursor of sphingosins, that forms the backbone of sphingolipids.
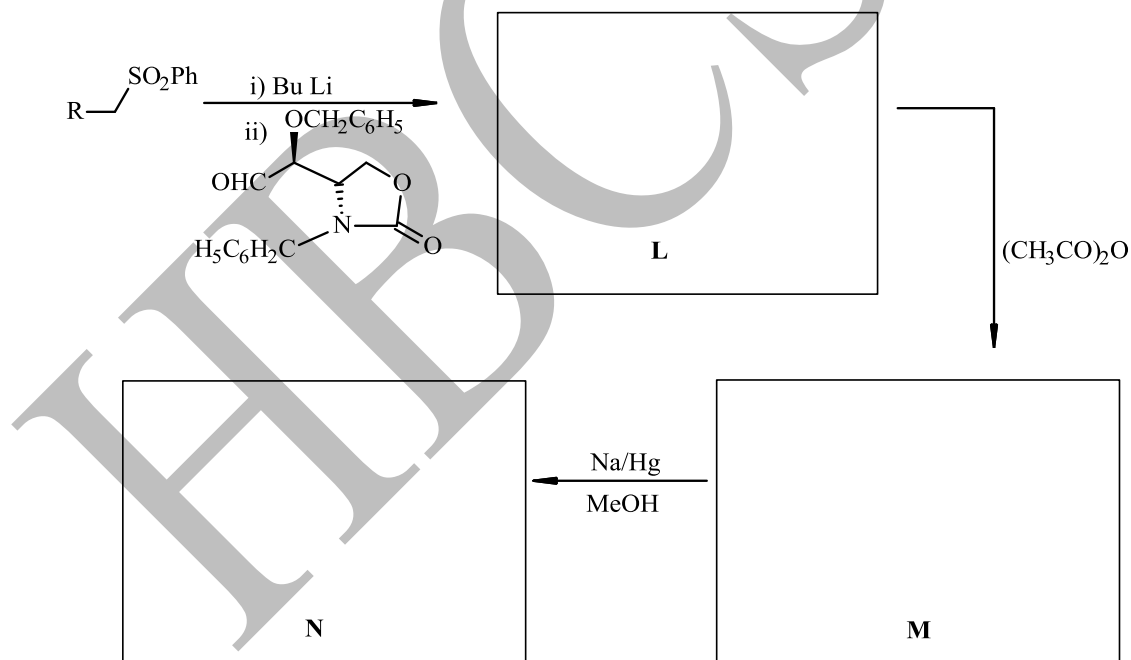
(2.5 marks)

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.

i)

ii)

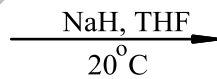**(3 marks)**

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 β - position.

2.8 Give the product of the following reaction.
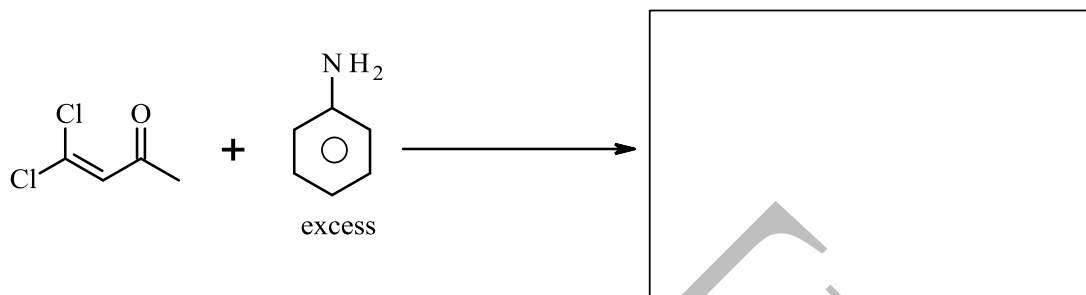
(1 mark)

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 BrO_3^- and Br^- in acidic solution results in the formation of Br_2 and H_2O and the rate law is given by,

$$r = -\frac{d\,[\,BrO_3^-\,]}{dt} = k\,[BrO_3^-]\,[Br^-]\,[H^+]^2$$

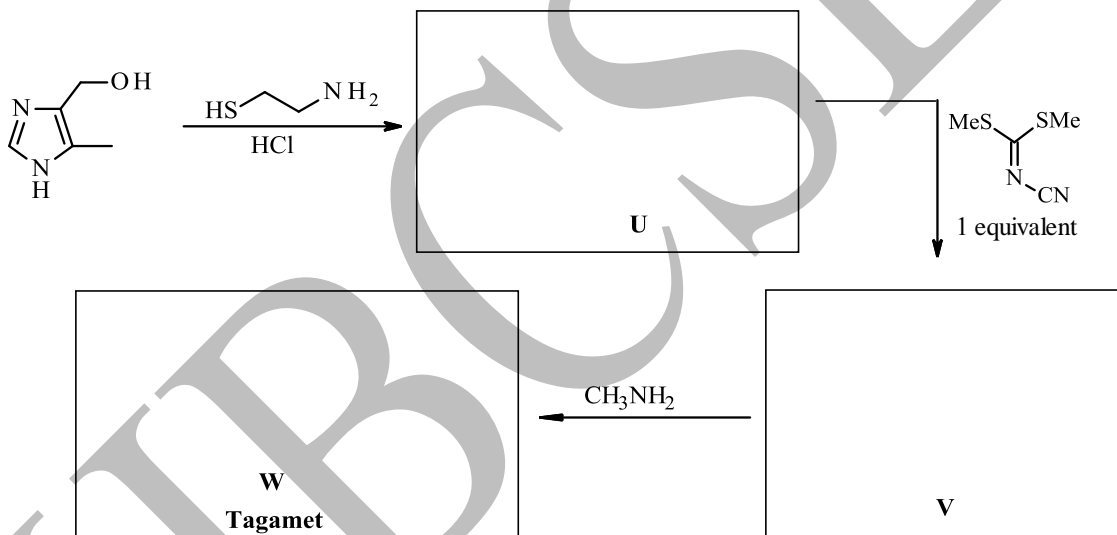**3.1**   Write the stoichiometric equation corresponding to this reaction.

(1 mark)

3.2   Write the total order of the reaction.

(1 mark)

3.3   Simplify the rate law for the same reaction if $[BrO_3^-]_0 = 2.5 \times 10^{-3}$ M, $[H^+]_0 = 1.0$ M   and $[Br^-]_0 = 0.28$ 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:

$Br_2 + C_6H_5OH \rightarrow BrC_6H_4OH + Br^-$
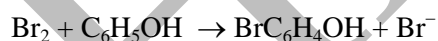
To detect the completion of the above monobromination reaction, the student added a drop of dilute methyl orange solution to the reaction flask. Methyl orange gets bleached by Br_2 and becomes colourless immediately even at very low Br_2 concentrations.

Monobromination of phenol, (C_6H_5OH) 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$_6$H$_5$OH] (M)	[Br$^-$] (M)	[H$^+$] (M)	[BrO$_3^-$]* (M)	Time taken for decolourization, t (sec)
1	4×10^{-3}	0.28	1.0	2.5×10^{-3}	11
2	2×10^{-3}	0.28	1.0	2.5×10^{-3}	4
3	1×10^{-3}	0.28	1.0	2.5×10^{-3}	1.5

*BrO$_3^-$ is added in the last just before starting the experimental run.

3.4 On doubling the concentration of C$_6$H$_5$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$_6$H$_4$OH started converting to Br$_2$C$_6$H$_3$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 $[BrO_3^-]_0$. In such an experiment, (mark **X** against the correct option/s)

(i) t will increase as $[BrO_3^-]_0$ increases

(ii) k can be obtained from the initial slope of $[BrO_3^-]$ vs t plot fit to an exponential curve

(iii) the experiment become less accurate as $[BrO_3^-]_0/[C_6H_5OH]_0$ decreases

(iv) t will be independent of $[Br^-]_0$

(v) k can be obtained using the slope of $1/t$ vs $[BrO_3^-]$ plot fit to a line

(2 marks)

Part B

3.7 Radioactive $^{238}U_{92}$ emits alpha and beta particles and forms stable $^{206}Pb_{82}$.

i) Write the balanced overall nuclear reaction.

(1 mark)

ii) An uranium ore sample is found to contain 1.19 g of $^{238}U_{92}$ and 1.03 g of $^{206}Pb_{82}$. (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 $^{238}U_{92}$ converts to $^{206}Pb_{82}$ in 1.0 billion years.

(1 mark)

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

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

(1.5 marks)

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

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

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.
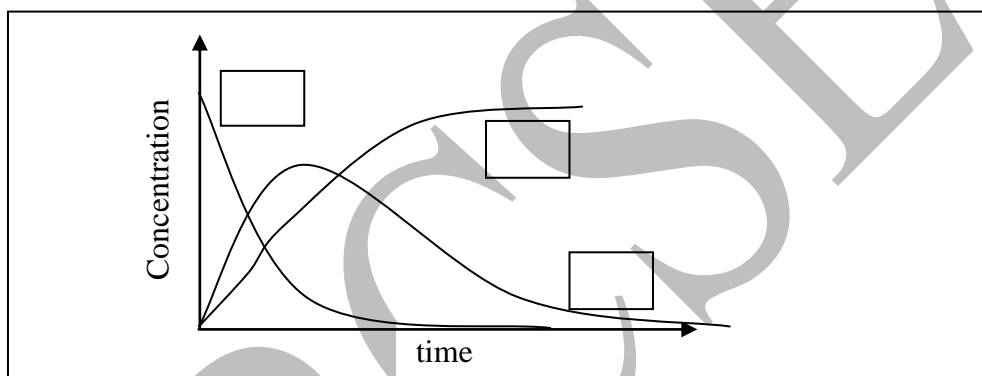
(1mark)

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

Nuclear disintegration rate approximately doubles for every 10^oC 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.

CD_2COOCH_3
CD_2COOCH_3

i) PhLi (excess)
ii) H_2O/H^+

A

CH_3COOD/D^+

B
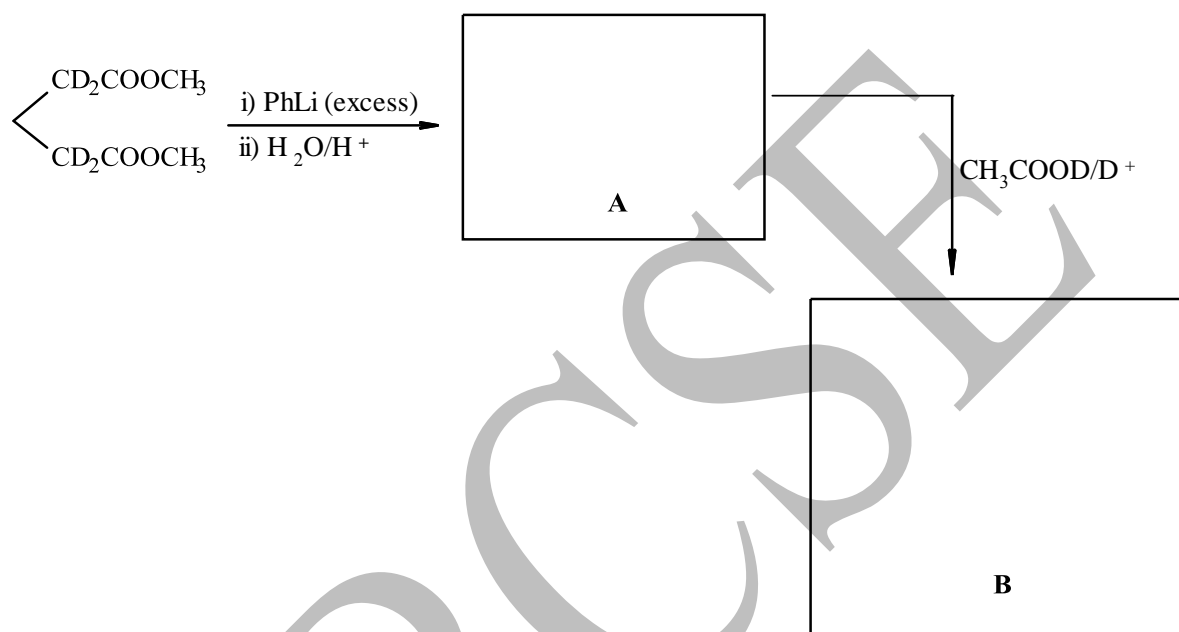
(1.5 marks)

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

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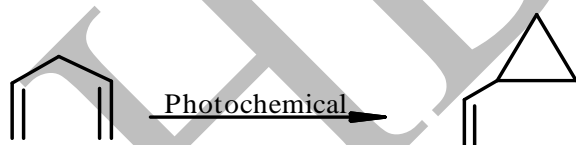
Zizaene is a naturally occurring terpene found in vetiver oil and used for the synthesis of α - vetivone that is used in perfumeries. It is prepared from compound **C**.

O

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 perfo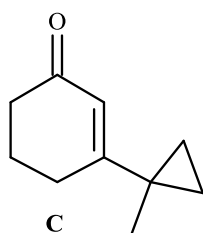rmed under thermal, photochemical or catalytic activation. Under thermal and photochemical conditions, this rearrangement proceeds via formation of the most stable biradical.
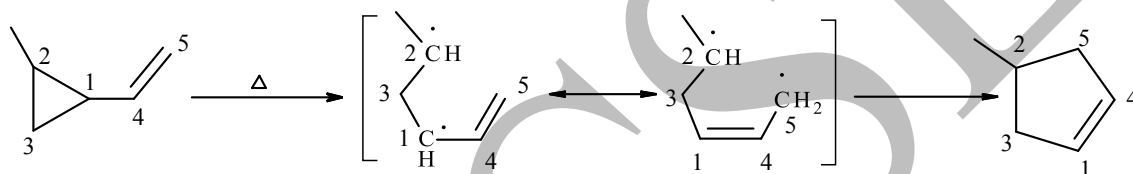
The vinyl cyclopropane rearrangement is a key step in the synthesis of Zizaene. The synthesis of Zizaene is outlined below.

4.3 Draw the structures of **D – F** in the following reaction sequence.
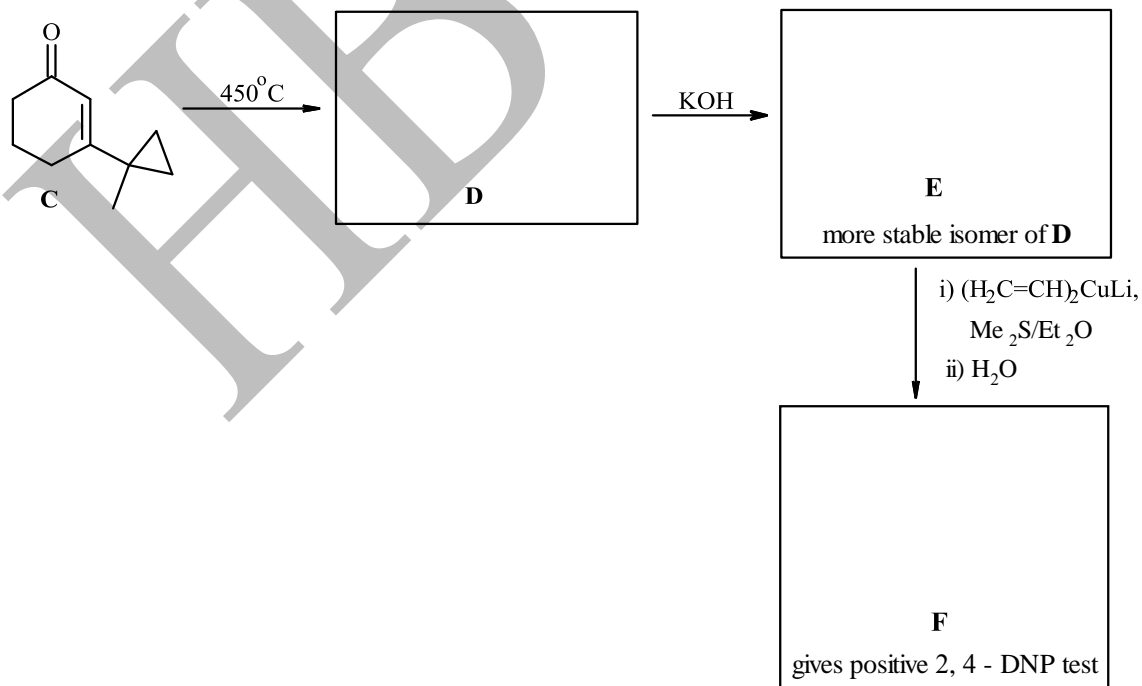
(2.5 marks)

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

$$F \xrightarrow[\text{ii) PhS-SPh}]{\text{i) LDA, THF}} G \xrightarrow[120\,^{\circ}\text{C}]{\text{NaIO}_4} [\text{H}] \longrightarrow I$$
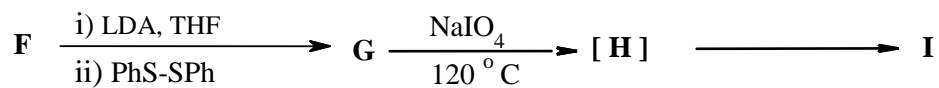
4.4   Identify **G**, **H** and **I**.

G	H Intermediate	I % C = 81.77 % H = 9.15

(2 marks)

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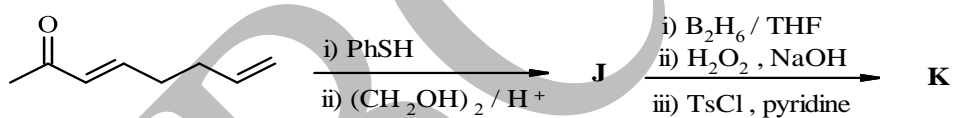
J	K

(3 marks)

Compound **N** is an intermediate for the synthesis of Zizaene. It is synthesized as shown below.
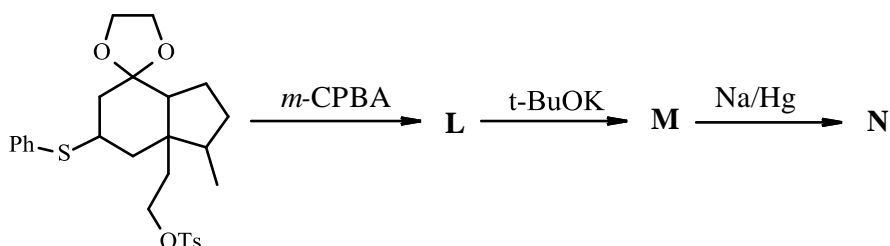
4.6 Identify **L**, **M** and **N**.

L	M	N
%C = 60.55 %H = 6.41 %O = 20.95		%C= 75.63 %H = 9.97

<div align="right">

(3.5 marks)

</div>

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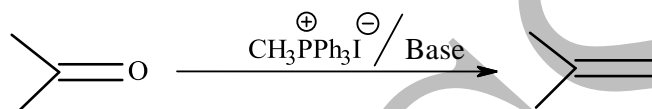
4.7 Identify **O** and **P.** Draw the structure of Zizaene**.**

O	P	Zizaene

<div align="right">

(3 marks)

</div>

4.8 How many stereocenters does Zizaene have?

<div align="right">

(0.5 marks)

</div>

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 Cu_2S and lower black layer of Ni_2S_3 remaining with the ore are then mechanically separated. The Ni_2S_3 is roasted in air to give a green solid (Step-II), which on subsequent treatment with water gas (mixture of CO and H_2 gas) at 50 ^{o}C gives a volatile complex and other byproducts (Step-III). This complex on thermal decomposition in air at 230 ^{o}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 H_2 from water gas reacts with Ni ions and reduces it   ☐
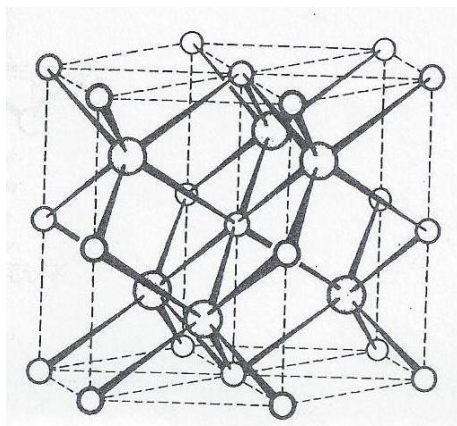
b) H_2 from water gas reduces Ni ions and then CO complexes with

        the reduced form of Ni   ☐

c)   Only CO from water gas reduces Ni ions   ☐

d)   Both CO and H_2 from water gas act as reducing agents   ☐

                                                                  (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, 5th 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			
Ni	6	4	Octahedral	Trigonal Prismatic	Square planar	Tetrahedral
As	6	4	Octahedral	Trigonal Prismatic	Square planar	Tetrahedral

(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, $CH_3C(NOH)C(NOH)CH_3$]. Nickel precipitates as a neutral complex ($C_8H_{14}O_4N_4Ni$), 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 ^{o}C are

a) $NiSO_4.7H_2O$ + excess NH_3 →   **X**   ln K = 8.61   Equation I

b) **X** + $2(H_2NCH_2CH_2NH_2)$ →   **Y**   ln K = 9.67   Equation II
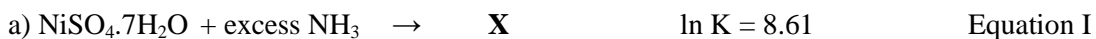
5.4 i) Draw the structure/s of all possible isomers of **Y** and **encircle** the optically active isomer/s if any.

(2 marks)

ii) Calculate the entropy change during the formation of **Y** in Equation II at 25 ^{o}C, if the heat of reaction for Equation II at constant pressure is -12.1 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, Li_2O, to give a black solid $Li_xNi_{1-x}O$ 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) $Li_xNi_{1-x}O$ exhibits both cationic and anionic vacancies

ii) $Li_xNi_{1-x}O$ 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 $1/8^{th}$ 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	Δ_0 (cm^{-1})	Δ_t (cm^{-1})
Co^{3+}	20,760	9,226
Fe^{3+}	14,000	6,220
Ni^{2+}	8,500	3,780

(Δ_0 and Δ_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
$NiFe_2O_4$		
$NiCo_2O_4$		

(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_2 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 $Ni(OH)_2$ 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 $KMnO_4$ 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 $KMnO_4$

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

Lanthanide Series

57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967

Actinide Series

89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]