Instructions for students

- Write your Name and Roll No. at the top of the first pages of all problems.

- This examination paper consists of 37 pages of problems including answer boxes.

- Total marks for INChO 2013 paper are 97.

- 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 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 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 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 4th February 2013.

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

Name of Student	Roll No.

**Problem 1**   **20 marks**

Free radicals

Carbon free radicals are trivalent carbon species containing an unpaired electron. They are involved in many synthetic, environmental and biochemical reactions. They are generated by photochemical, thermal or redox reactions through homolytic fission. Both electron donating and electron withdrawing groups stabilize a radical and such radicals are known as nucleophilic and electrophilic radicals respectively.

1.1   The correct order of stability for the following radicals is

(A) $(CH_3)_3C^{\bullet}$ (B) $CH_3CH_2^{\bullet}$ (C) $HC{\equiv}C^{\bullet}$ (D) $PhCH_2^{\bullet}$
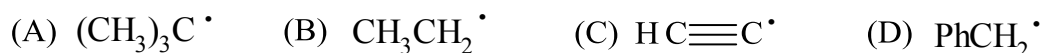
a) $A > B > C > D$ ☐   c) $D > A > B > C$ ☐

b) $B > D > A > C$ ☐   d) $C > A > B > D$ ☐

                                                                    (1 mark)

One of the common reactions which free radicals undergo is hydrogen abstraction to generate new radicals.

1.2   For the following compound, the correct order of ease with which hydrogen abstraction takes place from carbons numbered as 1 to 6 is
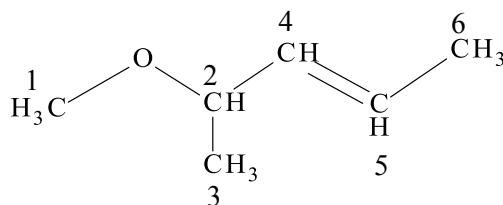
a) $2 > 6 > 4=5 > 1 > 3$ ☐   c) $1 > 2 > 6 > 3 > 4=5$ ☐

b) $2 > 1 > 6 > 3 > 4=5$ ☐   d) $6 > 1 > 2 > 4=5 > 3$ ☐

                                                                    (1.5 marks)

1.3   Halogenation of alkanes with molecular halogen in the presence of light takes place by radical mechanism. When n-butane is chlorinated with chlorine in the presence of light, the yields of 1-chlorobutane and 2-chlorobutane are 28% and 72% respectively. Calculate the ratio of relative reactivities of the hydrogens at C_1 and C_2 positions.

$C_1:C_2 =$

(1.5 marks)

1.4 The number of possible dichloro products, including stereoisomers formed when (S)-2-chlorobutane reacts with chlorine in presence of light is

a) 6 ☐   b) 3 ☐   c) 4 ☐   d) 5 ☐

(1mark)

1.5 Oxygen exists as a diradical and many organic compounds undergo air oxidation in the presence of light to give hydroperoxides. Draw the structure of the hydroperoxide (**A**) formed when tetrahydrofuran (THF) undergoes air oxidation.


THF $O_2 / h\nu$ **A**
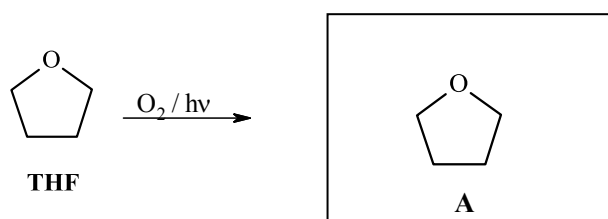
(1 mark)

1.6 Polyunsaturated fatty acids in oils undergo enzymatic air oxidation resulting in rancidity of the oils. Draw the structure/s of the product/s responsible for the rancidity of linoleic acid (the product contains conjugation)**.**

Linoleic acid $O_2 / enzyme$ **B**

B
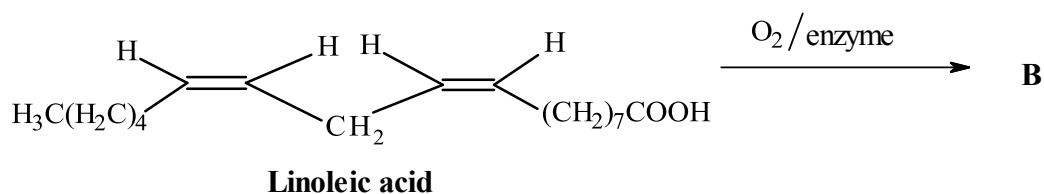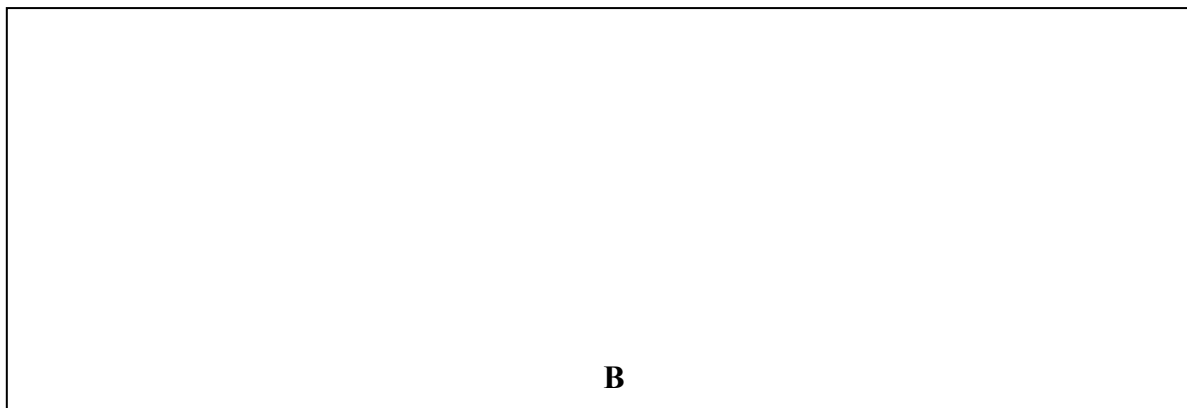
(1.5 marks)

1.7   An antioxidant like vitamin E is used as preservative for compounds that can undergo oxidation. Antioxidants react with radicals which are responsible for oxidation. Draw the structure of the radical **C** generated by the reaction of vitamin E with the radical RO•.
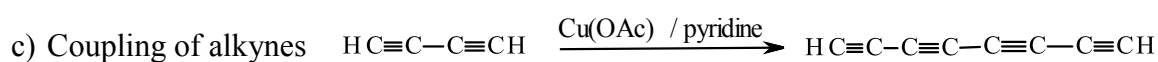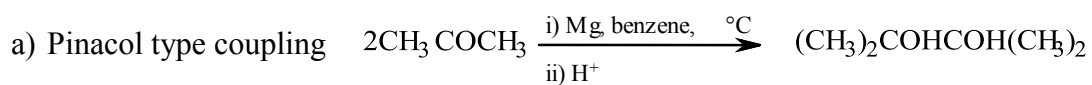

Vitamin E

$+$ RȮ $\longrightarrow$ **C**

C
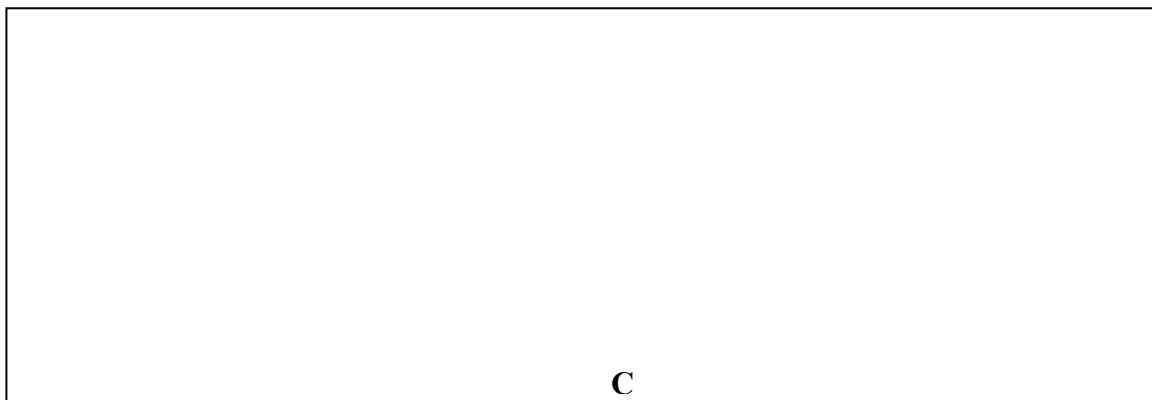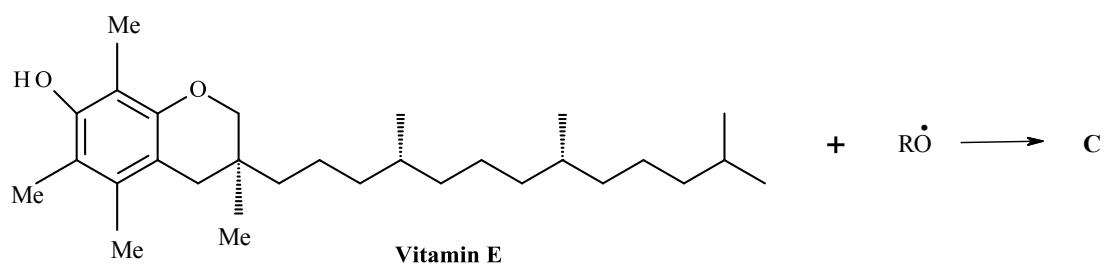
(1 mark)

1.8   Radical **C** in **1.7** is stable because of

a) hyperconjugation   c) steric hindrance

b) delocalisation   d) electromeric effect

(0.5 mark)

Dimerisation of radical intermediates generated by single electron transfer from metal ions are very useful in carbon-carbon bond formation. Some of them are given below

a) Pinacol type coupling $2CH_3COCH_3$ $\xrightarrow[\text{ii) H}^+]{\text{i) Mg, benzene, } °C}$ $(CH_3)_2COHCOH(CH_3)_2$

b) Acyloin condensation $2CH_3 \cdot COOC_2H_5$ $\xrightarrow[\text{ii) H}_3O^+]{\text{i) NaEt}_2O}$ $CH_3COCH(OH)CH_3$

c) Coupling of alkynes $HC{\equiv}C{-}C{\equiv}CH$ $\xrightarrow{\text{Cu(OAc)} / \text{pyridine}}$ $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}CH$

1.9   Suggest suitable starting compounds to prepare the compounds in i) and ii) below by a single step involving a radical intermediate.
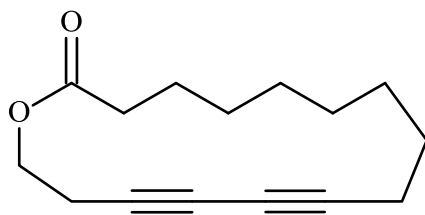
i)   Intermediate (**E**) which is used in the synthesis of anticancer drug taxol.
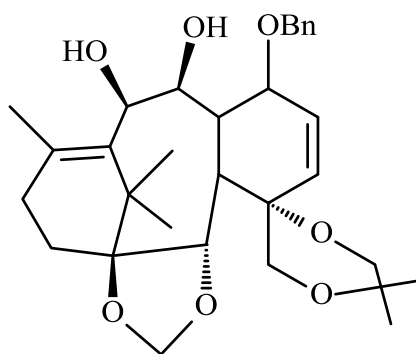
E

(1 mark)

ii) Intermediate (**F**) which is used in the synthesis of Exaltolide used in perfumes.


F

(1 mark)

Dehalogenation of an organic halide can be brought about via a radical reaction using tributyltin hydride (Bu$_3$SnH) and azobisisobutyronitrile (AIBN). AIBN acts as an initiator to generate Bu$_3$Sn$^{\bullet}$ radical which in turn reacts with RX to generate the alkyl radical R$^{\bullet}$ which is highly reactive. Bu$_3$SnH also acts as a hydrogen donor. (In general, formation of 5/6 membered rings is more favourable as compared to smaller/larger ring systems).
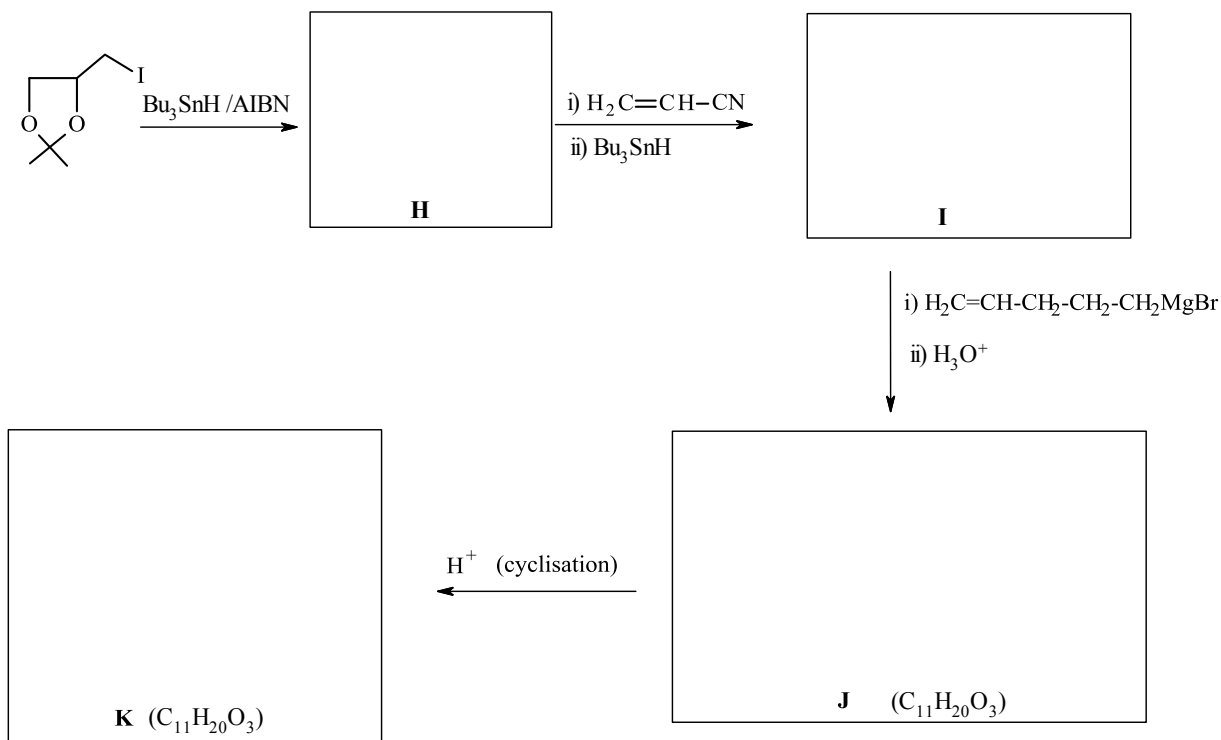
1.10 Give the structure of product **G** formed in the following reaction. One mole of **G** consumes one mole of hydrogen on hydrogenation.
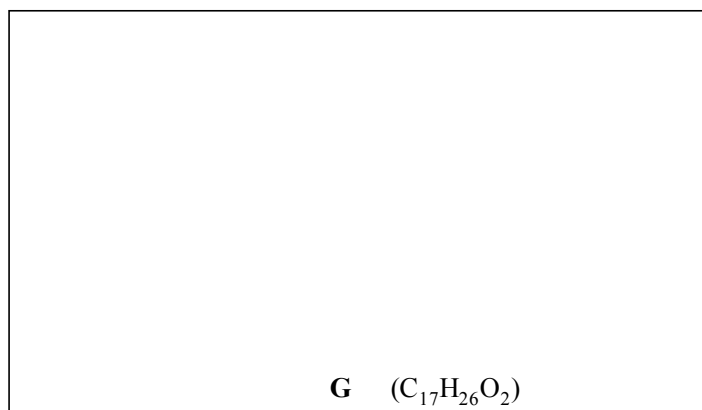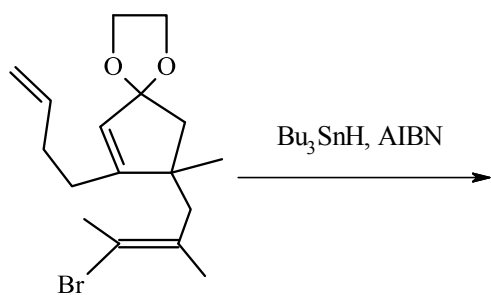

G   (C$_{17}$H$_{26}$O$_2$)

(1.5 marks)

1.11 The following synthesis yields a compound (**K**) that is responsible for the secretions of the glands of various bees and flies. Draw the structures of **H-K** (Compound **J** gives a orange red ppt with 2,4-DNP while **K** does not).

(4 marks)

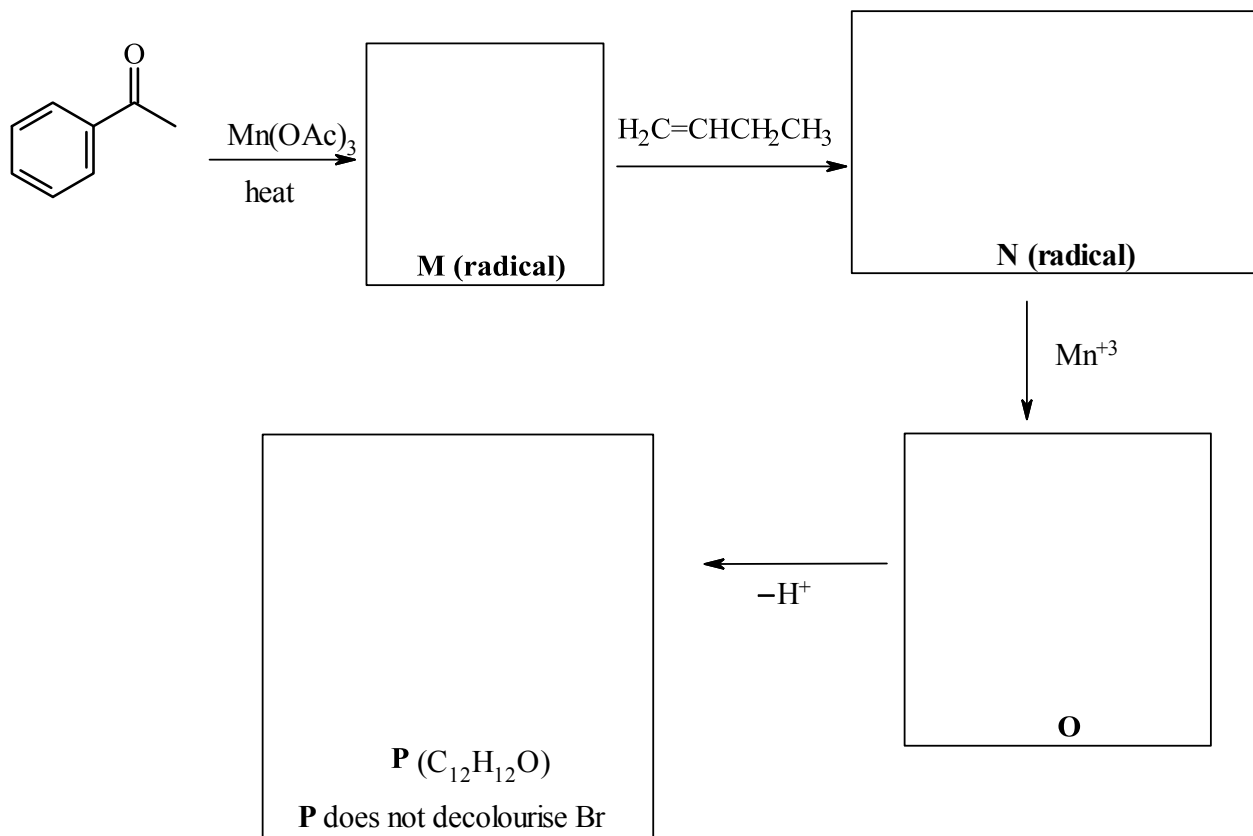**1.12** Mn(OAc)$_3$ is used as a single electron oxidant in C-C bond forming reactions. Metal ions (M^{n+}) in the higher oxidation state can abstract hydrogen to form radical.

$$R\text{-}CH_3 \xrightarrow{M^{n+}} R\text{-}\overset{\bullet}{C}H_2$$
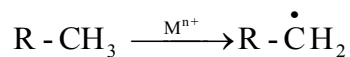
Metal ions (M^{n+}) can also abstract an electron from a radical to form carbocation.

Draw the structures of **M-P** in the following reaction scheme.

M (radical)

H$_2$C=CHCH$_2$CH$_3$ → **N (radical)**

Mn^{+3}

O

−H$^+$ →

P (C$_{12}$H$_{12}$O)

P does not decolourise Br

(3.5 marks)

Name of Student	Roll No.

Problem 2   **18 marks**

Transition Metal Chemistry

Carbon monoxide (CO) is a colorless, odorless and tasteless gas that is lighter than air and highly toxic to humans.

2.1   Draw the resonance structures (Lewis structures) of carbon monoxide (CO) and underline the one which follows the octet rule.
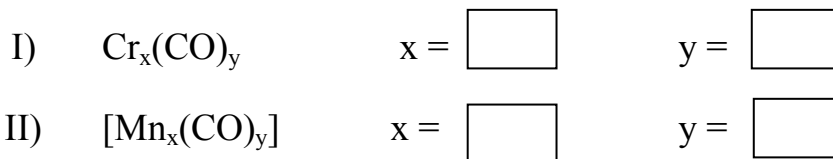
(1.5 marks)

Carbon monoxide forms many metal carbonyls with transition metals in which there is a Metal-Carbon bond.

2.2   Four possibilities of metal carbonyl bondings are given below, in which the metal (M) is in its lower oxidation state. Select the most favourable bonding type.
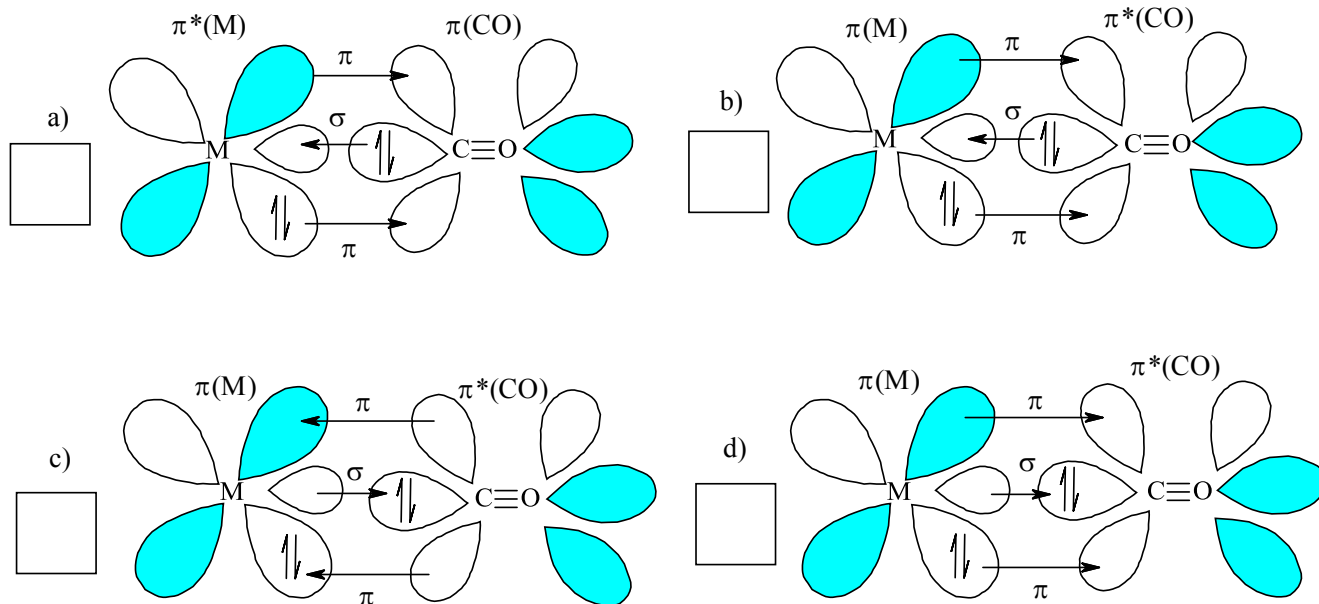
(1.5 marks)

2.3   Using the effective atomic number (EAN) rule identify the value of x and y metal carbonyls I and II, draw the structures of the metal carbonyls.

I) $Cr_x(CO)_y$ x = ☐   y = ☐

II) $[Mn_x(CO)_y]$ x = ☐   y = ☐

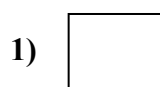I   II

(3.5 marks)

According to the Valence Bond Theory (VBT), the metal atom or ion under the influence of the ligands can use its (n-1)d, ns, np and nd orbitals for hybridization. These hybrid orbitals overlap with ligand orbitals that can donate electron pairs for bonding. The symbol ⇅ indicates electrons in metal and the symbol xx indicates electrons from the ligand. (Write approprite alphabets in the boxes)

2.4   Using VBT match the complexes (1-3) with appropriate hybridization schemes (a-c).

Complex   **Hybridization scheme**

1. $[Ni(CO)_4]$ a) | ⇅ | ⇅ | ⇅ | ⇅ | XX | | XX | | XX | XX | |

2. $[Ni(Cl)_4]^{2-}$ b) | ⇅ | ⇅ | ⇅ | ⇅ | ⇅ | | XX | | XX | XX | XX |

3. $[Ni(CN)_4]^{2-}$ c) | ⇅ | ⇅ | ⇅ | ↑ | ↑ | | XX | | XX | XX | XX |

1) ☐   **2)** ☐   **3)** ☐

(2 marks)

Metal carbonyls can be synthesized by disproportionation reactions wherein one part of the reactant is oxidised and the other part is reduced.

2.5   Write a balanced chemical equation of the reaction for the synthesis of nickel carbonyl from an appropriate cyanide.

                                                                         (1 mark)

The infrared stretching frequency in terms of wavenumber $\bar{\upsilon}$ and expressed in units of cm^{-1} is given as $\bar{\upsilon} = 1/(2\pi c)\sqrt{k/\mu}$ (where c is the velocity of light, k is force constant and μ is reduced mass).

2.6   Using the value of force constant as $1854 Nm^{-1}$, calculate the stretching frequency of free CO molecule.

                                                                         (2 marks)

A major consequence of the synergic bonding in metal carbonyls is the reduction in the bond order of the C-O bond which results in the lowering of the CO stretching frequency. Any effect which decreases C-O bond order should necessarily increase M-C bond order as the two are complementary to each other.

2.7   Arrange the given metal carbonyls according to the descending order of C-O stretching frequency. (Write approprite alphabets in the boxes)

i) a) MCO   b) M_2CO c) M_3CO

where M stands for metal.

☐ > ☐ > ☐

ii) a) $[Ni(CO)_3PMe_3]$ b) $[Ni(CO)_3PF_3]$ c) $[Ni(CO)_3PPh_3]$

☐ > ☐ > ☐

(1.5 marks)

2.8   With respect to the complex $Co_2(CO)_8$ answer the following. In the IR spectrum, this complex in the solid form shows separate bands, above and below 2000 cm^{-1}.

i)   Draw the structure of the complex in the solid form.

ii)   When it is dissolved in hexane the bands below 2000 cm^{-1} disappear. Draw the structure of the complex in the solution.

(2 marks)

Hydroformylation (Oxo process) is the conversion of olefins to aldehydes catalyzed by cobalt and rhodium carbonyl complexes. A catalytic cycle for the hydroformylation of a terminal olefin is given below and the steps in this cycle are labeled from 1 to 7.
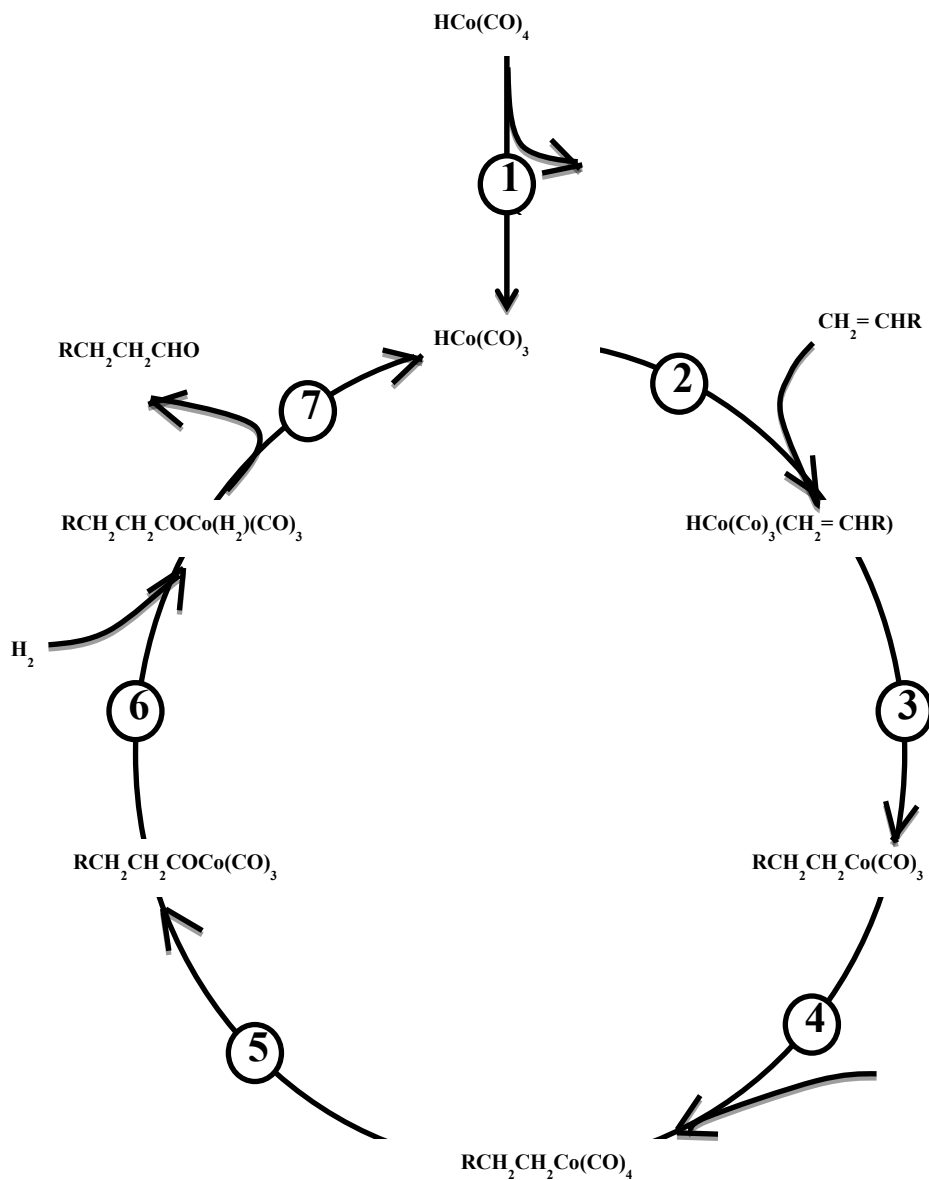
2.9   The steps given in the diagram can involve any of the following reactions:

a) ligand substitution and dissociation b) reductive elimination c) π- olefin coordination d) olefin insertion e) oxidative addition f) alkyl migration.

Using the given information, complete the following table.

Step No.	Reaction type (Choose from the above list and write only the alphabet)	Formal oxidation state of **metal** in the product obtained at the **end** of the step	Number of d electrons
3			
6			
7			

(3 marks)

Name of Student	**Roll No.**

Problem 3   **14 marks**

Synthesis of natural products

Natural products have played a pivotal role in the development of Organic Chemistry. Synthesis of a natural product by an unequivocal route is used to establish its structure.

A commercially important natural product **A** forms an orange–yellow precipitate with 2,4-DNP reagent. It does not react with $[Ag(NH_3)_2]NO_3$ solution. **A** on reduction with $NaBH_4$ gives a secondary alcohol and on oxidation with nitric acid yields a dicarboxylic acid containing the same number of carbon atoms. On bromination, **A** gives a monobromo product.

3.1   On the basis of above observations, **A** contains (Mark X in the correct box/es)

(a) aldehydic carbonyl ☐   (b) ketonic carbonyl ☐

(c) ester carbonyl ☐   (d) no unsaturation ☐

(e) C=C ☐

(1 mark)

Oxidation of **A** with nitric acid gives **B** ($C_{10}H_{16}O_4$) and further oxidation of **B** gives **C** ($C_9H_{14}O_6$).

3.2   78 mg of **B** ($C_{10}H_{16}O_4$) requires 15.6 mL of 0.05 M KOH for complete neutralization and 85 mg of **C** ($C_9H_{14}O_6$) requires 23.4 mL of 0.05 M KOH for complete neutralization. Calculate the number of acidic functional groups present in **B** and **C**.

(1 mark)

Perkin Jr. and Thorpe synthesised **C** ($C_9H_{14}O_6$) using methyl acetoacetate as per the reaction sequence presented below.

3.3   Identify and draw the structures of the reagent **(P)** and intermediate products **(D, E)** and compound **C**. (An α-haloester and zinc metal react to form an organozinc reagent analogous to the Grignard reagent.)
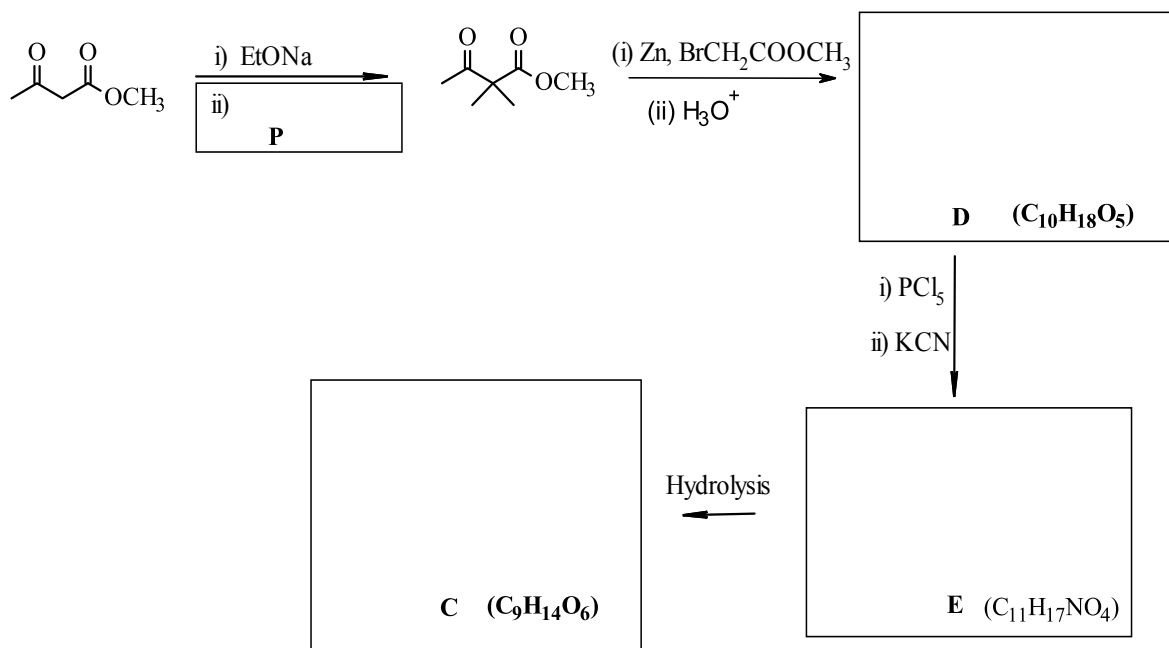
(3 marks)

3.5   Draw the Fisher projection formula/e of possible stereoisomers of **C** and assign the proper stereodescriptor/s.
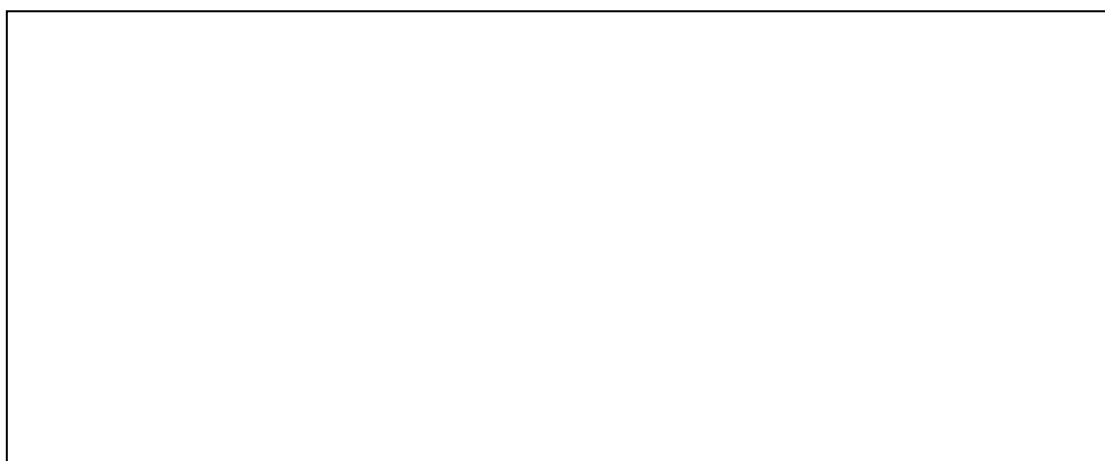
(1.5 marks)

3.6   Compound **H** is an intermediate required for the synthesis of **A**. It is synthesised from diethyl malonate by the following route. Identify reactant **Y**, intermediates **F**, **G** and compound **H**.

$$CH_2(COOC_2H_5)_2 \xrightarrow[\text{ii)}]{\text{i) EtONa}} \boxed{Y}$$

Structure with $COOC_2H_5$ and $COOC_2H_5$ groups, two methyl groups, and a ketone (=O).

i) Ba(OH)$_2$

ii) H$_3$O$^+$

$$\boxed{H} \quad + \quad \boxed{G} \xleftarrow[\text{ii) HCl}]{\text{i) NaOBr}} \boxed{F\ (C_8H_{12}O_2)}$$
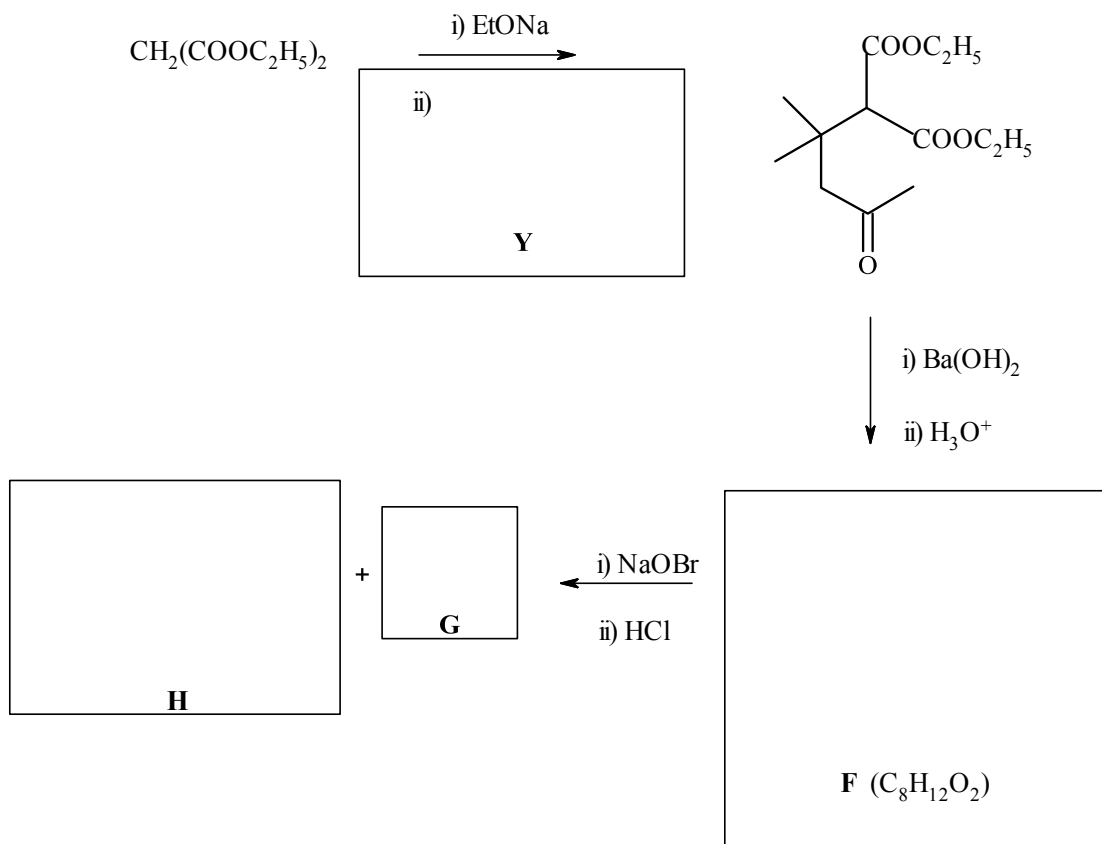
(3.5 marks)

3.7   Diethyl 3,3-dimethyl pentanedioate is used to prepare **B** ($C_{10}H_{16}O_4$) as follows. Draw the structures of compounds **I, J, K** and **B.**

—COOC$_2$H$_5$

—COOC$_2$H$_5$

+

COOC$_2$H$_5$

COOC$_2$H$_5$

$\xrightarrow{C_2H_5ONa}$

I

i) EtONa

ii) CH$_3$I(1 mole)

K   (C$_{14}$H$_{24}$O$_6$)

$\xleftarrow{NaBH_4}$

J (C$_{14}$H$_{20}$O$_6$)

HI

COOH

COOH

i) HBr

ii) Zn / CH$_3$COOH

B   (C$_{10}$H$_{16}$O$_4$)
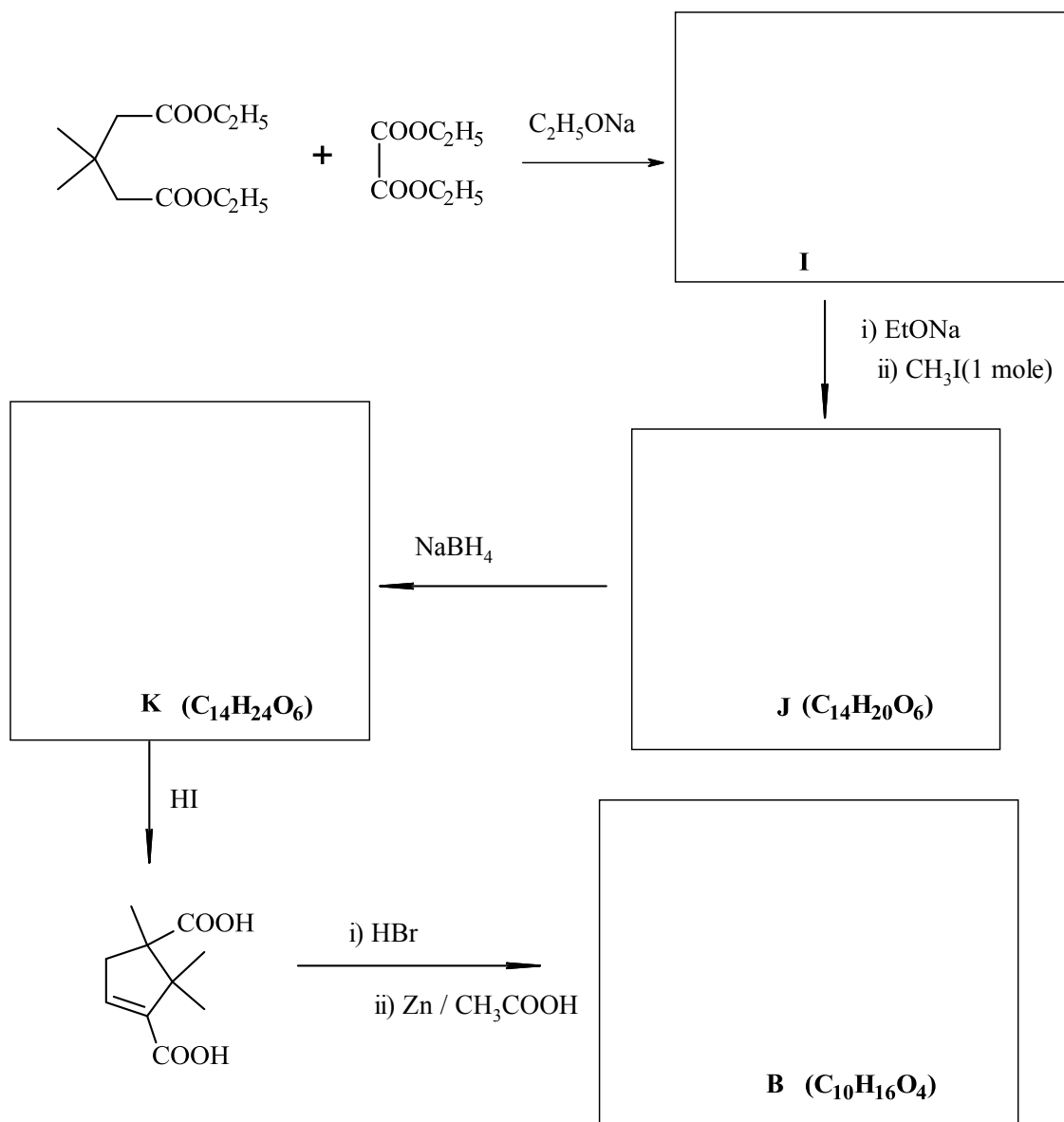
(3 marks)

3.8   The IUPAC name of **(B)** is

(1 mark)

Name of Student	**Roll No.**

Problem 4   **18 marks**

Hydrogen as a fuel

A.   The rapid depletion of fossil fuels has inspired extensive research in the area of alternate and renewable energy sources. Of these, hydrogen is the most contemplated fuel of the future. However, cost effective production and hazard free storage are major issues in using H_2. (**Note: Use the data in table 1 given at the end of Part A, wherever necessary).**

4.1   A cylinder contains hydrogen at a pressure of 80MPa at 25°C. Assuming ideal behaviour, calculate the density of hydrogen in the cylinder in kg/m^3.

                                                                        (1 mark)

4.2   Assuming complete combustion, calculate heat of combustion when

        (i) 1 g of hydrogen and (ii) 1 g of carbon are burnt.

                                                                        (1 mark)

4.3   1kg of hydrogen is burnt with oxygen at 25°C and the heat energy is used for different purposes. Using this heat, calculate

        (i) the maximum theoretical work.

        (ii) work that can be produced by a heat engine working between 25°C to 300°C. (The efficiency of a heat engine = work done/ heat absorbed = $[1- (T_{low}/T_{high})]$ where T is in K)

(2 marks)

4.4   If the maximum theoretical work (calculated in **4.3(i)**) is used to run an electric motor

of 1Watt, under standard potential conditions,

(i) for how many months the motor will run?

(ii)What is the value of the current produced by this motor? (Assume 30 days in all

months.)

(2 marks)

Table 1

	H₂ (g)	**O₂ (g)**	**H₂ O (l)**
$S°_{298K}$ / J mol K^{-1}	131	205	70
	H₂O (l)	**CO₂ (g)**	
ΔH_f^0 / kJmol^{-1}	−286 kJmol^{-1}	−394 kJmol^{-1}	

B. One method to produce hydrogen on an industrial scale is the reaction of methane with overheated water vapour at 1100 K to form hydrogen and carbon monoxide. The reaction is known as 'steam reforming'.

4.5 Write the balanced equation for the steam reforming of methane

(0.5 mark)

4.6 The K_P of the reforming reaction at 1100K is 28.6. When 1 kmol of methane and 1 kmol of water are reacted at 1100K, calculate the percentage conversion of methane at equilibrium at a total initial pressure of 1.6 bar.

(2 marks)

In another experiment, 1.0 kmol of CH_4 and 1.0 kmol of H_2O are taken in a sealed vessel at 400 K and 1.6 bar. The temperature is raised to 1100 K.

4.7   Calculate the pressure in the vessel at 1100 K and the % conversion of methane.

(2 marks)

C.   Heat engines and refrigerators

A heat engine is a system that converts heat into mechanical work. A heat "source" generates thermal energy that brings a working substance to a high temperature. The working substance then generates work in the engine while transferring heat to a sink at a lower temperature. The working of a heat engine is shown figure 1.
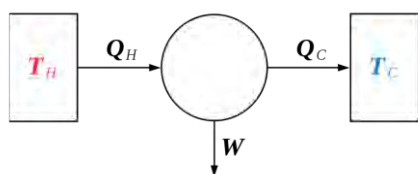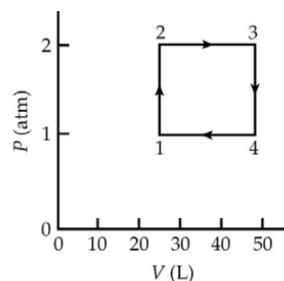
(Figure 1)   (Figure 2)

Heat engines can be modelled using thermodynamic cycles. The heat engine given in Figure 2 is of a working substance which is 1.00 mol of a monatomic ideal gas. The thermodynamic cycle begins at the point designated as '1' and goes clockwise and the values of P and/or V at each point is as given below: $P_1 = 1.00$ atm and $V_1 = 24.6$ L; $P_2 = 2.00$ atm; $V_3 = 49.2$ L; $P_4 = 1.00$ atm.

4.8   Calculate T_1, T_2, T_3 and T_4.

(2 marks)

**4.9**   Calculate ΔE for the paths i) 1→   ii) → 3   iii) 3→4   iv) 4→1
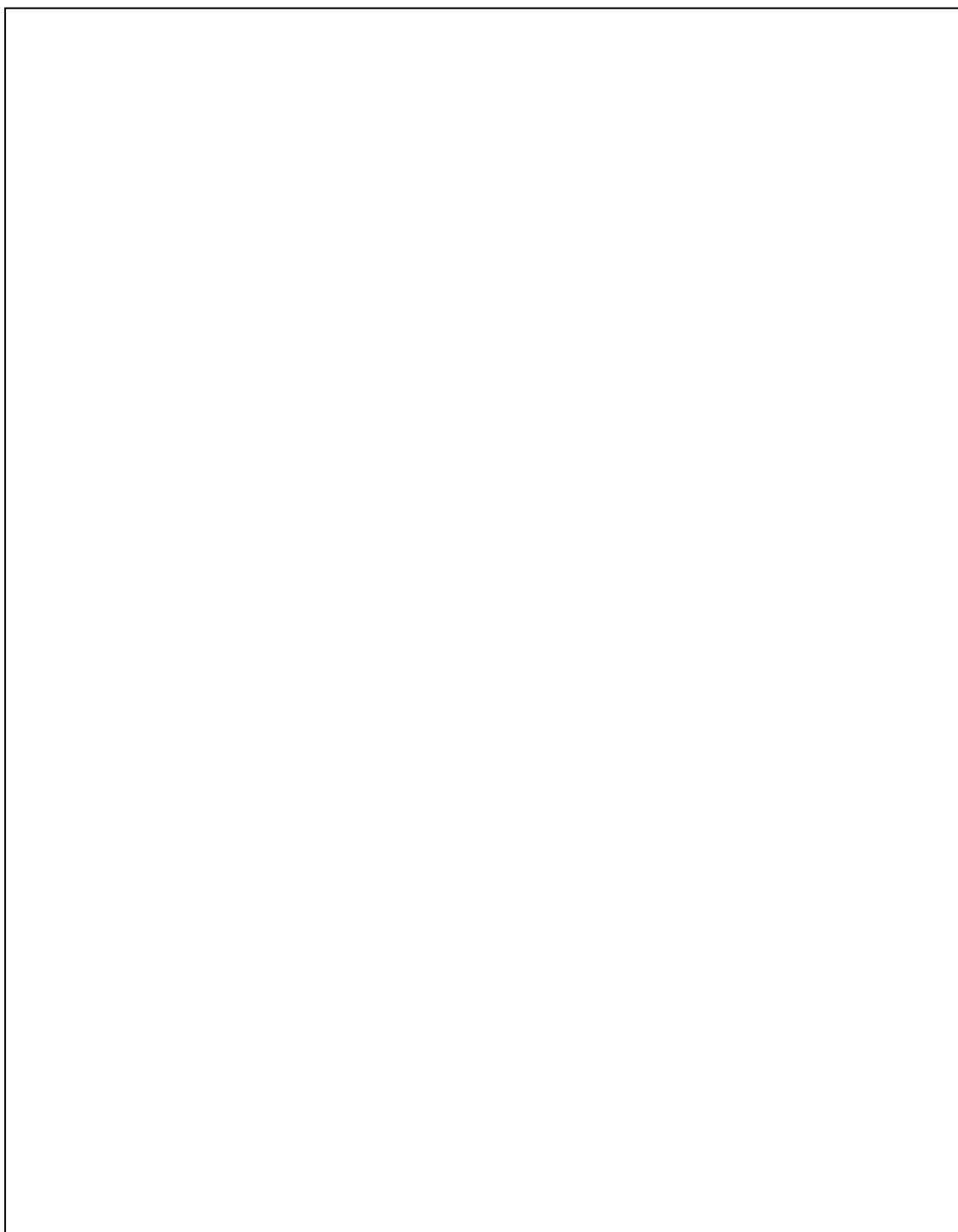
(2 marks)

The heat engine depicted in this problem is a 'Carnot heat engine' and the thermodynamic cycle of operations of this engine is known as a 'carnot cycle', named after Saudi Carnot, an engineer cum thermodynamist. The efficiency of a carnot

engine is defined as $(1- T_1/T_2)$ where T_1 and T_2 are the temperatures of the sink and the source.

4.10   Calculate the efficiency of the cycle given in figure 2.
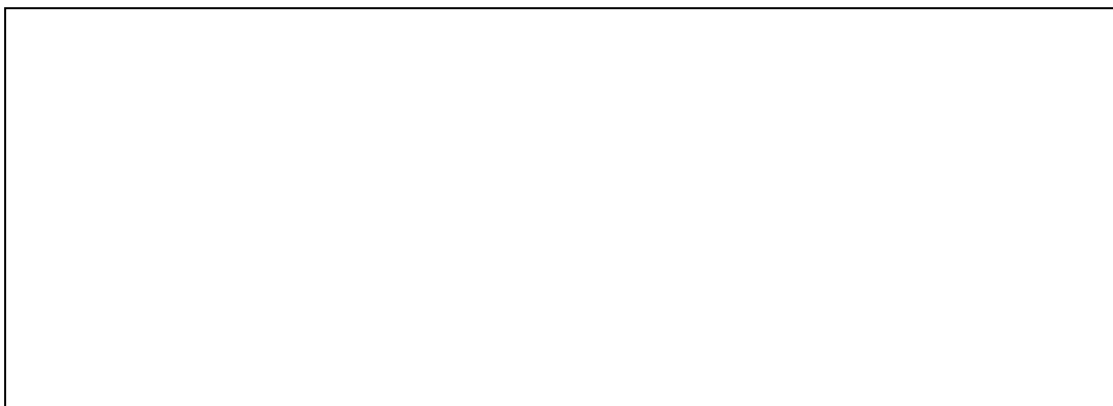
(1.5 marks)

Another system completes a cycle consisting of six quasi-static steps, during which the total work done by the system is 100 J. During step 1 the system absorbs 300 J of heat from a reservoir at 300 K, during step 3 the system absorbs 200 J of heat from a reservoir at 400 K, and during step 5 it absorbs heat from a reservoir at temperature T_3. Steps 2, 4, 6 are adiabatic such that the temperature of one reservoir changes to that of next.

4.11   a) What is the entropy change of the system for the complete cycle?

       b) If the cycle is reversible, what is the temperature T_3?
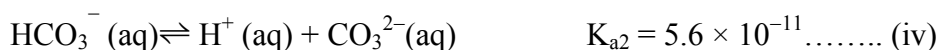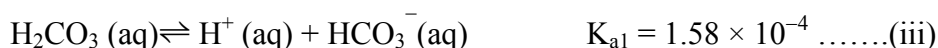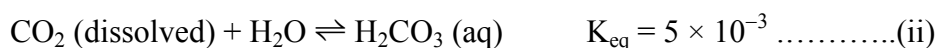

(2 marks)

Name of Student	**Roll No**

Problem 5   **15 marks**

Acid-Base Equilibria

The transport of gases through circulation is an important function of blood in the body. CO_2 generated in our body dissolves in the blood and is in equilibrium with CO_2 in gas phase. A complete representation of CO_2 buffer system in the body is shown below.

CO_2 (g) $\rightleftharpoons$ CO_2 (dissolved) $K = 3.01 \times 10^{-5}$ …………..(i)

CO_2 (dissolved) $+ H_2O \rightleftharpoons H_2CO_3$ (aq) $K_{eq} = 5 \times 10^{-3}$ …………..(ii)

H_2CO_3 (aq) $\rightleftharpoons H^+$ (aq) $+ HCO_3^-$ (aq) $K_{a1} = 1.58 \times 10^{-4}$ …….(iii)

HCO_3^- (aq) $\rightleftharpoons H^+$ (aq) $+ CO_3^{2-}$ (aq) $K_{a2} = 5.6 \times 10^{-11}$ …….. (iv)

When p_{co_2} is expressed in terms of mm Hg, the values of K, K_{a1} and K_{a2} given above are at 37° C **.**

5.1   Calculate the value of overall equilibrium constant K_a', for the equilibrium between $[H^+]$(aq), $[HCO_3^-]$ (aq) and CO_2 dissolved.

                                                          (1 mark)

In *vivo*, the (HCO_3^-/CO_2) is an open system in which $[CO_2]_{dissolved}$ is maintained constant and any excess CO_2 produced by the reaction

H^+(aq)$+ HCO_3^-$ (aq) $\rightarrow CO_2 + H_2O$ is expelled out by the lungs. This reaction is responsible for maintaining the pH of blood. We will understand the effectiveness of this open system through the following example:

A total carbonate pool (essentially $[HCO_3^-]+ [CO_2]_{(dissolved)}$) in blood plasma is 2.52×10^{-2} M.

5.2   i) The pH of blood in the body is maintained at 7.4. What is the ratio of $[HCO_3^-]/[CO_2]$ and   the concentration of each component present at pH 7.4?

(2 marks)

ii) What would be the pH of the blood if 5×10^{-3} M H$^+$ is added under conditions where the increased [CO$_2$] cannot be exhaled out?

(1.5 marks)

iii) What would be the pH if 5×10^{-3} M [H$^+$] is added and the increased [CO$_2$] is exhaled out? (thereby the original [CO$_2$] does not change)

(0.5 mark)

5.3   If a person exhales 274 mL min^{-1} of CO$_2$ at 37^{0}C and 101.3 kPa pressure, calculate [CO$_2$] and [HCO$_3^-$] in CO$_2$ rich blood. (Blood flows through the lungs at a rate of 5.4L min^{-1})
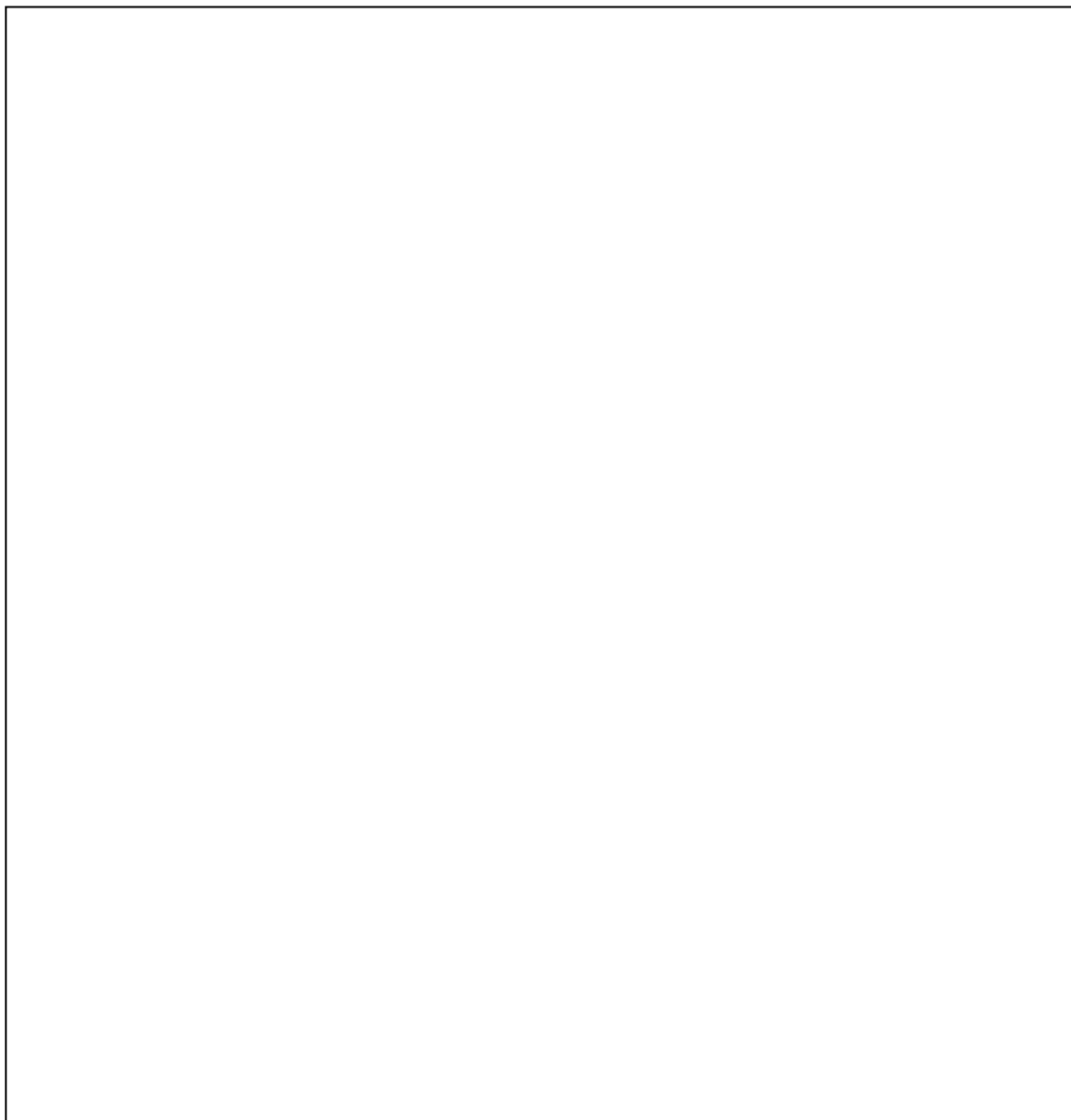
(3 marks)

In the body, haemoglobin binds with O_2. The O_2 binding curves for haemoglobin in presence and absence of CO_2 is qualitatively sketched below. The curves indicate percent saturation of haemoglobin by O_2 as a function of partial pressure of O_2.
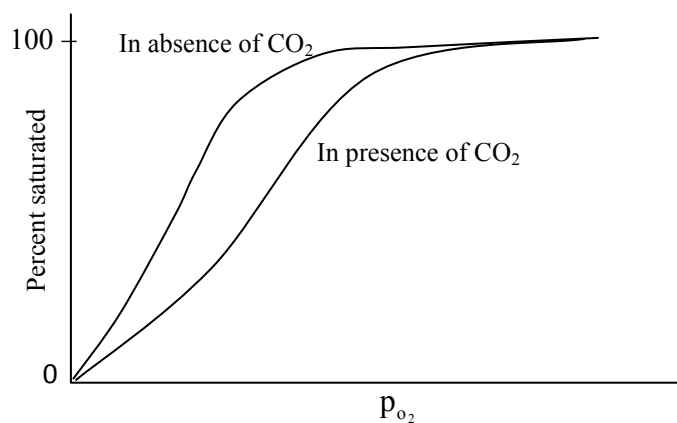
5.4   Which of the following statement/s is/are correct for the given curves?

      i)   In presence of CO_2, higher p_{o_2} is needed for a given percent saturation   ☐

      ii)   In presence of CO_2, lower p_{o_2} is needed for a given percent saturation   ☐

      iii) In absence of CO_2, maximum saturation of haemoglobin occurs at lower p_{o_2} ☐

      iv) In absence of CO_2 for any given percent saturation, higher p_{o_2} is needed   ☐

                                                       (1 mark)

Each Haemoglobin (Hb) molecule can take up four molecules of O_2. In the following figure oxygenated fraction of haemoglobin is plotted as a function of oxygen pressure in kPa. The curves in the figure are for different types of haemoglobin, namely, normal (curve 1) and abnormal (curves 2 and 3). (O_2 pressure in lungs, and muscles is 15 kPa and 2 kPa respectively.)
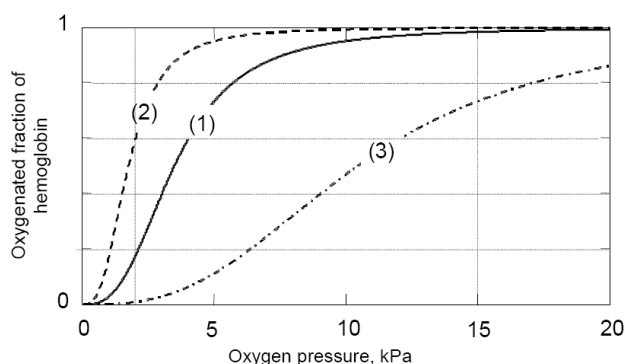

Figure 1

5.5   Using the figure given above, calculate the number of moles of O_2 absorbed in muscle tissues when one mole of (Hb) travels from the lungs to the muscles and back again, in all three types of (Hb) shown in the figure.

                                                       (1 mark)

In intense physical activity, lactic acid is produced in the muscles, particularly in an anaerobic metabolism. High lactic acid/lactate ($[HL]/[L^-]$) levels in muscles lead to high acidity and destruction of other metabolites. In blood, lactic acid (HL) ($K_{HL}=1.4 \times 10^{-4}$) is neutralised by the bicarbonate present in the blood.

5.6   Calculate the pH of blood in muscles when the lactic acid concentration is
2.70 x 10^{-3}M.

(1 mark)

5.7   Calculate the equilibrium constant for the reaction between lactic acid and
bicarbonate. Write the equations for the appropriate equilibria involved. (For this
calculation, assume the dissociation constants of H_2CO_3 as $K_{a1}=4.5 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$).

(2 marks)

5.8   Blood also contains Ca (II) ions. Determine the maximum concentration of calcium
ions that can be present in blood at pH = 7.4.

([HCO_3^-] = 0.022 M at this pH and for simplification assume that only Ca will
precipitate as $CaCO_3$. Ksp of $CaCO_3$ = 4.9 x10^{-9})

(2 marks)

Name of Student	**Roll No.**

Problem 6   **12 marks**

Electrochemistry

Electrochemistry encompasses synthesis of molecules, analysis of diverse and trace materials and also technological applications such as fuel cells and batteries. Electrochemical potential is a key parameter of electrochemistry. Walther Nernst, a Nobel prize winning German physicist cum chemist, formulated a valuable equation that relates the actual reversible potential of an electrode to its standard reversible potential E°, a thermodynamic quantity.

I   For all the calculations, assume i) concentration can be used in place of activity. ii) The temperature of the electrochemical cells is 25^oC, unless specified otherwise.

II   Use **Table I** given at the end of this problem of electrochemical potentials to solve the problems.

6.1   For the cell $Ag_{(s)} \mid Ag_2SO_{4(s)} \parallel H_2SO_4 \mid H_2 \, (1 \, atm) \mid Pt$

a) Write the half cell reactions and the overall reaction.

(1.5 marks)

b) Calculate E of the cell if $E^°$ is -0.627V and the concentration of H_2SO_4 is 0.1M.

(0.5 mark)

c) Which of the following statement/s is/are true for the given cell?

 i) The given cell requires a salt bridge

ii) The given cell does not require a salt bridge

iii) It is not possible to draw current from the cell as represented

iv) It is possible to draw current from the cell as represented

(1 mark)

6.2   For the cell, $Ag_{(s)} | Ag_2SO_4$ (0.02M) $\|$ $CdSO_4$ (0.016M) $| Cd_{(s)}$

a) Calculate the equilibrium constant at 25^oC for the overall cell reaction

(1.5 marks)

b) Which of the following statement/s is/ are correct for the above cell?

i) E will be less negative at 35º C

ii) E will be more negative at 25º C

iii) E does not change with temperature

(1 mark)

6.3   Using the data in **Table I**

a) Calculate the equilibrium constant for the reaction, $Cu_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons 2Cu^+$

(2 marks)

b) What is the equilibrium concentration of Cu^+ ions when excess $Cu_{(s)}$ is added to 0.01M Cu^{2+} solution?

(1 mark)

6.4   A solution of 0.01M $SnCl_2$ and 0.1M KCl was suspected to contain $PbCl_2$. The lead content was determined by electrodeposition using a Pt cathode and a Ag /AgCl anode. The electrolysis was stopped when the Sn just started to deposit on the cathode (the shiny metallic lustre of Sn makes it visually possible).

a) Write the cell reaction for the deposition of Pb.

(0.5 mark)

b) Calculate the final Pb^{2+} concentration in the solution.

(3 marks)

Table I

Redox system (aq)	Electrode potential at 25°C (V)	Redox system (aq)	Electrode potential at 25°C (V)
Ag^+/ Ag	0.800	Pb^{2+}/ Pb	-0.126
Cd^{2+}/ Cd	-0.400	Sn^{2+}/ Sn	-0.140
Cu^+/ Cu	0.521	Cu^{2+}/Cu	0.339