Name of Student **Centre**

Problem 1 **13 Marks**

Chemical Kinetics and Reaction Rates

Nitric oxide [nitrogen (II) oxide] is the first gas to have been identified as a messenger in mammals and as an intermediate in the production of nitric acid. It has a role in air pollution and is essential to maintain the blood pressure.

In a reaction of oxidation of nitric oxide by oxygen, the rate law does happen to reflect the reaction stoichiometry. Experimentally it is observed to be overall a third order reaction.

1.1 Predict two **simple** possibilities of the rate law expressing the rate (v), in terms of appropriate powers of the reactant concentrations.

v = or v =

(1 mark)

1.2 With respect to the rate laws given by you, write the balanced chemical equations assuming that they reflect reaction stoichiometry.

Chemically correct reaction from the above two is

(1.5 marks)

1.3 Express the reaction rate in terms of the time derivatives of concentration of each of the gaseous components of the correct equation.

v =

(1 mark)

Two mechanisms are suggested for the correct stoichoimetric reaction.

1.4 Mechanism – 1

$$NO(g) + O_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3\,(g) \quad \text{(Fast pre-equilibrium)}$$

$$NO_3(g) + NO\,(g) \xrightarrow{k_2} 2NO_2\,(g) \quad \text{(Slow)}$$

Use the equilibrium concentration of $[NO_3]$ (from the first step) to derive the rate law for the formation of $[NO_2]$.

(2 marks)

1.5 Mechanism - 2

$$NO(g) + NO\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2\,(g)$$

$$N_2O_2\,(g) + O_2\,(g) \xrightarrow{k_2} 2\,NO_2\,(g) \quad \text{(with very large value of } k_{-1}\text{)}$$

Steady state approximation is used for N_2O_2 (i.e. its rate of formation equals rate of consumption). Obtain the rate law within this approximation. State the assumption used.

(2 marks)

1.6 How will you experimentally compare the two mechanisms?

(1 mark)

1.7 The oxidation reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ attains equilibrium at 230°C. The concentrations of various species at equilibrium are found to be $[NO] = 5.42\times10^{-2}$ M, $[O_2] = 12.7\times10^{-2}$ M, and $[NO_2] = 15.5$ M. Calculate the equilibrium constant (K_c) of the reaction at this temperature.

(1 mark)

1.8 Assume that all the gases involved in the reaction in **1.7** show ideal behavior. Calculate the change in internal energy of the reaction at 1 atm and 25°C. The enthalpy change of the reaction at the given condition is −114.0 kJ.

(1 mark)

1.9 Predict whether the entropy change (ΔS) of the process in **1.7** is positive, negative or zero, when the reaction proceeds to completion.

(0.5 mark)

1.10 The rate limiting step of a reaction which is catalyzed by H^+(obtained from the ionization of a weak acid, e.g. acetic acid) is $H^+ + R \rightarrow B$, and the catalyst is regenerated in a subsequent rapid step. Considering the ionization constant of the weak acid, predict the dependence of the reaction rate on the concentration of acid.

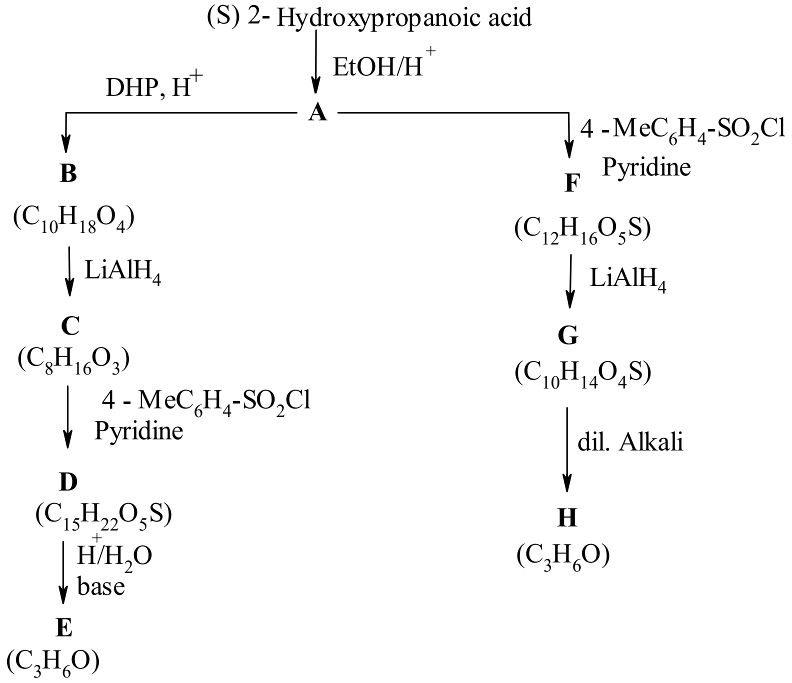
(2 marks)

Name of Student **Centre**

Problem 2 **16 marks**

Pheromones – A Case of Sulcatol

The chemicals used by living organisms for intra-species communication are called “pheromones”. They are secreted in minute quantities. Normally a specific stereoisomer only is active; the other stereomer/s may be inactive or even inhibitor. “Sulcatol” is an ambrosia beetle aggregation pheromone. It is active only as a 65:35 mixture of its enantiomers and hence the enantiomers are synthesized separately and mixed in right proportion. The use of readily available chiral natural products, called “chiral synthons”, as starting compounds in the synthesis of complex chiral compounds is called “chiral pool strategy”. (S)-lactic acid is one such chiral synthon. The enatiomers **E** and **H** of Sulcatol are prepared through stereospecific reactions from (S)-lactic acid (2-hydroxypropanoic acid), as shown below

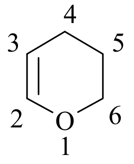


2.1 Draw the structures of (S) 2-hydroxypropanoic acid and **A**.

(S) -2-hydroxypropanoic acid **A**

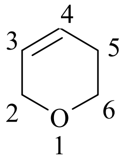
(1.5 marks)

During a sequence of reactions, sensitive functional groups are often protected using "protective groups". Dihydropyran (DHP) is used to protect a hydroxyl group, as the corresponding THP derivative can be prepared easily and after the crucial reaction, can be hydrolyzed under mild acidic conditions to the hydroxyl derivative. The conversion **A** → **B** requires the involvement of such a step. Two isomeric dihydropyrans **I** and **J** exist.



I

or



J

2.2 Which of them **(I or J)** would be suitable for the formation of DHP derivatives of alcohols?

☐

(0.5 mark)

2.3 Which position of the selected DHP would couple with –OH group?

☐

(0.5 mark)

2.4 Draw the structures of compounds **B** and **C**.

(1.5 marks)

2.5 The role of pyridine in the conversion **A** → **F** is

(i) to remove chloride ion from 4-Me-C_6H_4-SO_2Cl ☐

(ii) to displace hydroxyl group ☐

(iii) to increase nucleophilicity of hydroxyl group ☐

(iv) to act as a weak nucleoplile ☐

(0.5 mark)

2.6 Draw the structures of compounds **D** and **F**.

(2 marks)

Compounds **E** and **H** do not give 2,4-DNP derivatives.

2.7 Draw the structures of **E** and **H**, specifying their stereochemical descriptors.

(2.5 marks)

Another reactant **O** is prepared by the following sequence –

$$CH_3CHO \xrightarrow[\text{(ii) acetone}]{\text{(i) LDA, -78}^{0}\text{C, THF}} \mathbf{K} \xrightarrow{\text{mild acid}} \mathbf{L} \xrightarrow{LiAlH_4} \mathbf{M} \xrightarrow{PBr_3} \mathbf{N} \xrightarrow[\text{ether}]{Mg} \mathbf{O}$$

2.8 Identify compounds **K** to **O**.

(3 marks)

O is reacted separately with **E** and **H** followed by hydrolysis, to obtain isomers **P** and **Q** of Sulcatol.

2.9 Draw the structures of compounds **P** and **Q**.

(2 marks)

The PMR data of compound **M** is given below: 1.62 (3H), 1.68(3H), 4.15 (d, 2H), 5.45 (broad s, 1H). Besides these there is a additional broad peak, which disappeared on D_2O addition.

2.10 Draw the structure of **M** and assign the chemical shifts to different protons.

(2 marks)

Name of Student	**Centre**

Problem 3 **16 Marks**

Sea Water

In polar regions, life exists below the frozen crust of ice. Only the top layer of the ocean is frozen and the ice floats on water.

3.1 The density of ice differs from that of water because

(a) ice is a solid and water is a liquid ☐

(b) hydrogen bonding exists only in water ☐

(c) ice has an open cage-like structure ☐

(d) ice is covalently bonded but water involves ionic bonding ☐

(1 mark)

3.2 Sea water contains many salts such as halides and sulphates of sodium, potassium, magnesium, calcium etc. Hence, sea water freezes at a temperature lower than the freezing point of pure water. The freezing point of a typical sample of sea water is –1.94°C at 1 atm. Calculate the boiling point of sea water at 1 atm.

K_f (water) = 1.86 K molal^{-1}, K_b (water) = 0.51 K molal^{-1}.

Boiling point of pure water at 1 atm is 373.1 K

(2 marks)

3.3 The van't Hoff factor *i* is a measure of association.

$$i = \frac{\text{no. of particles after association}}{\text{no. of particles before association}}$$

(A) van't Hoff factor for 0.1 M aqueous sodium chloride is 1.87. The van't Hoff factor for 0.1 M magnesium sulphate is expected to be

(a) 1.87 ☐

(b) 1.25 ☐

(c) 1.92 ☐ **(1 mark)**

(B) In magnesium sulphate the ionic interaction

(a) is same as that observed in NaCl ☐

(b) is weaker than that observed in NaCl ☐

(c) is stronger than that observed in NaCl ☐

(d) is not responsible for the *i* value ☐

(1 mark)

3.4 Sea water is a rich source of halides. However, the concentration of iodide is less than that of the other halides, as the iodide ions are absorbed by the sea weeds and stored as iodine. Iodine can be extracted from sea weeds. The distribution of iodine between two immiscible solvents is given by the distribution ratio (D), which is constant at a given temperature.

$$D = \frac{\text{Conc. of } I_2 \text{ in solvent } 1}{\text{Conc. of } I_2 \text{ in solvent } 2}$$

(A) One litre of an aqueous solution containing 0.127 g of iodine was shaken with 10 ml of CCl_4. Certain amount of iodine was extracted into the organic layer. The organic layer was found to be 0.0465 N with respect to iodine. If another extraction was performed with 10 mL of CCl_4, what mass of iodine will be left in water layer? Atomic mass of iodine is 127.

(3 marks)

(B) The solubility of iodine in aqueous KI is far higher than that in water due to the formation of the triiodide ion. Give the hybridization of the central atom of the triiodide ion and show the geometry of the bonded pairs of electrons.

(2 marks)

3.5 In an attempt to desalinate sea water containing sodium, magnesium, calcium and potassium ions as the only cations, the total cation content of the sea water was estimated. 10 mL of a sample of sea water was diluted to 1L. The cations were replaced by hydrogen ions and the salts were converted to their corresponding mineral acids using the ion exchange resin zerolit 225. The exchange of ions increases with increase in the valency as well as the size of cations exchanged. 100 mL aliquot of the diluted sample was passed through the cation exchanger zerolit 225 and the sample obtained from the exchanger required 32 mL of 0.05 M NaOH for exact neutralization. Molar mass of calcium carbonate = 100.

One may obtain total cation concentration in terms that of Ca^{2+} or any of its salts.

(A) Express the total salt content of sea water in terms of g L^{-1} of $CaCO_3$.

(1.5 marks)

(B) If the cations retained in the resin are washed using dilute HCl, which would be the first to come out of the ion exchange resin?

(0.5 mark)

(C) Total exchange capacity of the resin zerolit is 5 eq of the solute per gram of the resin. If 4 g of resin was used in the determination cited above, what % of active sites of the resin undergoes ion exchange?

(1 mark)

3.8 At a certain place sea water is found to be 0.6 M with respect to NaCl and 0.05M with respect to $MgCl_2$. It is concentrated by a manufacturer of common salt to get 4.8M solution with respect to NaCl and he wants to precipitate pure common salt by passing HCl gas. What is the minimum volume of HCl in L at STP that must be passed to initiate the salting out of NaCl from 1L of the solution? (K_{sp} of NaCl = 36)

(3 marks)

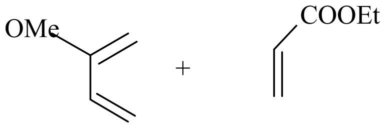
Name of Student	**Centre**

Problem 4 21 marks

Cycloaddition Chemistry

The Diels-Alder reaction is highly fascinating for synthetic organic chemists. Using this reaction one can build six membered carbocyclic and heterocyclic rings. The reaction has many interesting stereochemical dimensions. Otto Diels and Kurt Alder received Nobel Prize in 1950 for the discovery of this reaction. In this reaction, a conjugated diene reacts with a compound containing an activated multiple bond to form the adduct.

4.1 Draw the structures of all the possible products of the following reaction (No stereochemical features are to be shown)

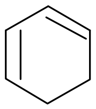


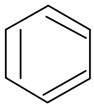
(1.5 marks)

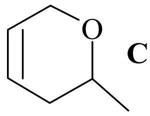
4.2 For any of the products in **4.1**, draw the structures of the stereoisomers possible.

(1.5 marks)

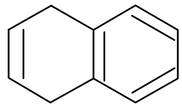
4.3 A few molecules (**A-D**) are shown below. Identify the molecules which can be synthesized through one-step Diels-Alder reactions and draw the structures of the possible reactants/intermediates for each of them.


A


B



C


D

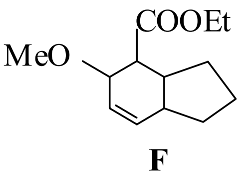
(4 marks)

A dicarboxylic acid **E** ($C_4H_4O_4$) on reaction with bromine gives a dibromoderivative ($C_4H_4Br_2O_4$), which is optically inactive.

4.4 Identify **E**. Draw the structure/s, with stereochemistry, of the product/s of the reaction of **E** with cyclopentadiene.

(2.5 marks)

Compound **F** can be prepared through an intra-molecular Diels-Alder reaction of **G**.

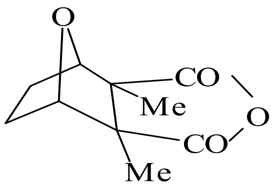


F

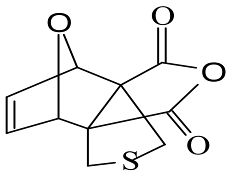
4.5 Draw the structure of compound **G**.

(1.5 marks)

Cantharidin (**H**) is a biomolecule isolated from a Spanish fly. **I** is the intermediate, which is prepared through a Diels-Alder reaction.



H



I

4.6 Draw the structures of the two components of the reaction leading to **I**.

(2 marks)

4.7 Write the reagent which will convert **I** into cantharidin **(H)**.

(1 mark)

4.8 Draw the structure of dimethyl 1,2-cyclobutene dicarboxylate (**J**).

(0.5mark)

When **J** is heated with maleic anhydride (butenedioic anhydride), an unusual reaction takes place to form compound **K**. When **K** is boiled with aq. NaOH and the solution is acidified, compound **L** ($C_{10}H_{10}O_8$), which is optically inactive, is obtained. 1.0g of **L** reacts with 77.5 mL of 0.2 M NaOH.

4.9 Equivalent weight of compound **L** is **(1 mark)**

4.10 The number of –COOH groups present in compound **L** is

(0.5 mark)

4.11 **L** is expected to contain (**Mark X for all the appropriate choices**)

(i) cyclobutane ring ☐

(ii) cyclohexane ring ☐

(iii)open chain structure ☐

(iv)one double bond ☐ **(1 mark)**

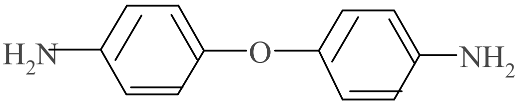
4.12 Draw a possible structure/s of compound **L** and compound **K**.

(2 marks)

4.13 Draw the structure of a possible intermediate in the reaction.

(1 mark)

L on heating forms **M** ($C_{10}H_6O_6$), which on reaction with **N** gives a polymer **O**.



N

4.14 Draw the structure of a representative segment of polymer **O**.

(1 mark)

Name of Student	**Centre**

Problem 5 21 marks

Acetylene – Production, Structure & Uses

Acetylene is an important industrial gas. It is used as a fuel and as a raw material in the production of organic compounds such as acetaldehyde, acetic acid, acetone and vinyl monomers. It has wide applications in neoprene rubber and vinyl resin industries.

Acetylene gas can be produced using calcium carbide and water according to the following reaction

$$CaC_2 + 2H_2O \xrightarrow{\qquad\qquad} C_2H_2 + Ca(OH)_2$$

A commercial sample of calcium carbide is 97% pure (3% inerts, which do not react with water). Acetylene is stored in a cylinder at 101.3 kPa pressure and at 27°C.

5.1 What is the density of acetylene gas at the above conditions?
(Assume that C_2H_2 behaves like an ideal gas)

(1 mark)

5.2 Calculate the amount of calcium carbide needed to produce 10m^3 of acetylene gas at the above mentioned conditions?

(2 marks)

5.3 For the production of $10m^3$ of acetylene gas, calcium carbide is treated with excess of water. A slurry containing $Ca(OH)_2$ and inerts in water is produced as the waste. If the mass percentage of water in the slurry is 80%, what is the mass of water initially added and what is the mass of final slurry?

(3 marks)

5.4 The standard heats of formation (in kJ mol^{-1}) of a few compounds are given below.

CH_4 (g)	-74.4	$H_2O(l)$	-285.5
C_2H_2 (g)	228.2	CO_2 (g)	-393.5

Compare the heat liberated when 16 kg of methane are completely burnt in excess of oxygen with that when 16 kg of acetylene is burnt.

(2 marks)

5.5 Describe the hybridization of all the carbon atoms in ethylene, acetylene and allene ($CH_2 = C = CH_2$) molecules.

(2 marks)

5.6 The C-H bond lengths in acetylene, ethylene and ethane molecules are 1.059Å, 1.086 Å and 1.093 Å respectively. This difference may be attributed to

a) decreasing p character on increasing unsaturation ☐

b) increasing p character with increasing unsaturation ☐

c) increasing s character with increasing unsaturation ☐

d) decreasing s character on increasing unsaturation ☐

(1 mark)

5.7 Acetylene is soluble to a large extent in acetone. This may be attributed to the weak interactions between acetone and acetylene. Which of the hydrogen is expected to be more acidic?

Hydrogen in the CH_3 group of acetone ☐

Hydrogen in acetylene ☐ **(0.5 mark)**

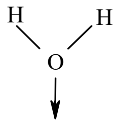
What are the molecules that have a non zero dipole moment?

acetylene ☐ water ☐

acetone ☐ ethylene ☐

(2 marks)

The dipole moment vector of water may be represented by the following diagram with the arrow pointing in the direction of the negative charge.



Show the dipole moment vector of acetone.

(0.5 mark)

One may now imagine the structure of the weakly bound 1:1 acetone – acetylene complex in their binary mixture. For this purpose you may consider the most acidic hydrogen interacting with the electron rich region of the other molecule. Draw the structure of such a complex indicating weak interactions with dotted lines.

(2 marks)

5.8 A catalyst has been developed for the conversion of acetylene into acetaldehyde. On the surface of the catalyst, the following reaction occurs

$$C_2H_2 + H_2O \xrightarrow{\text{cat}} CH_3CHO$$

The products contain small amounts of H_2, O_2 and CH_3COOH. The following reactions are assumed to be responsible for these products.

$$H_2O \longrightarrow H_2 + ½\, O_2$$

and $CH_3CHO + \frac{1}{2} O_2 \longrightarrow CH_3COOH$

In a typical experiment, C_2H_2 and $H_2O(g)$ are taken in a molar proportion of 1:1. Only a part of C_2H_2 is consumed in the reaction. In the final products, the ratio of $C_2H_2 : CH_3COOH$ is found to be 15:1 and $C_2H_2 : CH_3CHO$ is 5:3. Calculate the percentage conversion of C_2H_2.

(3 marks)

5.9 In the above example, in the final products $H_2 : O_2$ is found to be 5:1. What percentage of water initially supplied undergoes decomposition?

(2 marks)

Name of Student	**Centre**

Problem 6 **33 marks**

Transition Metal Chemistry

The transition metals form complexes that involve central metal atom coordinated with ligands. The geometry of these complexes depends upon the number of ligands associated with the central metal atom. Hexacoordinate metal complexes normally prefer to have octahedral geometry.

6.1 For each of the following combinations of metal-ligands complexes, draw structures of the possible isomers. Mark optical isomers by (*). For each case, label the drawn structures with appropriate stereodescriptors (eg. *cis, trans, mer, fac*). For case (iii) name the relationship that exists between the isomers.

(i) MX_4Y_2 (ii) MX_3Y_3 (iii) $M(en)_2X_2$ (en: ethylenediamine) Represent en by $\cap$

(7 marks)

One of the theories, viz, the valence bond theory (VBT),that explains bonding in co-ordination complexes was developed by Linus Pauling. It states that coordinate compounds contain complex ions in which ligands form coordinate bonds with the metal. The bond is formed by using a lone pair of electrons available on the ligand and an empty orbital of suitable energy available from the metal. This theory focuses on the atomic orbital from the metal that is used for bonding. It is useful in predicting shape and stability of the complex.

6.2 For the following complexes, using VBT, draw the orbital diagrams indicating the distribution of electrons in the base atom as well as central metal atom in the complex. Also predict the hybridization and geometries for each complex.

(i) $Fe(CO)_5$

(ii) $Ni(CO)_4$

(4 marks)

Though VBT was partly successful in predicting geometry, it has many limitations. For example, lack of obvious means of predicting whether a 4- coordinate complex will be tetrahedral or square planer. Crystal field theory (CFT) was developed by Bethe and van Vleck, overcomes these limitations and also accounts for color and spectra of the complexes. Depending on extent of d orbitals splitting, ligands are arranged in a sequence called as spectrochemical series. Generally the splitting pattern observed is as follows: halide donor < oxygen donor < nitrogen donor < carbon donor.

6.3 Based on the above information, draw the splitting of d orbitals indicating the distribution of electrons for the central metals in the following complexes and calculate magnetic moment for paramagnetic complex/es.

(i) $K_4[Co(CN)_6]$ and (ii) $K_4[Co(ox)_3]$

(4 marks)

6.4 Consider the diamagnetic complex $[M(en)_3](ClO_4)_3$ wherein M is a first row transition metal. Answer the following questions for the given complex.

i) Oxidation state of M ☐

ii) Number of d electrons present ☐

iii) Identify M ☐

iv) Whether this complex will be strong oxidizing agent

Yes ☐ No ☐

State the reason for your answer

(v) Draw all possible stereoisomers of this complex. (Indicate optically active isomer by (*), if any)

(6 marks)

6.5 From the following pair of oxides, indicate the number of d electrons of central metal atom. Also indicate which oxide will be colorless and which will be colored. Explain your answer in brief.

(i) TiO_2 and (ii) Fe_2O_3.

(2 marks)

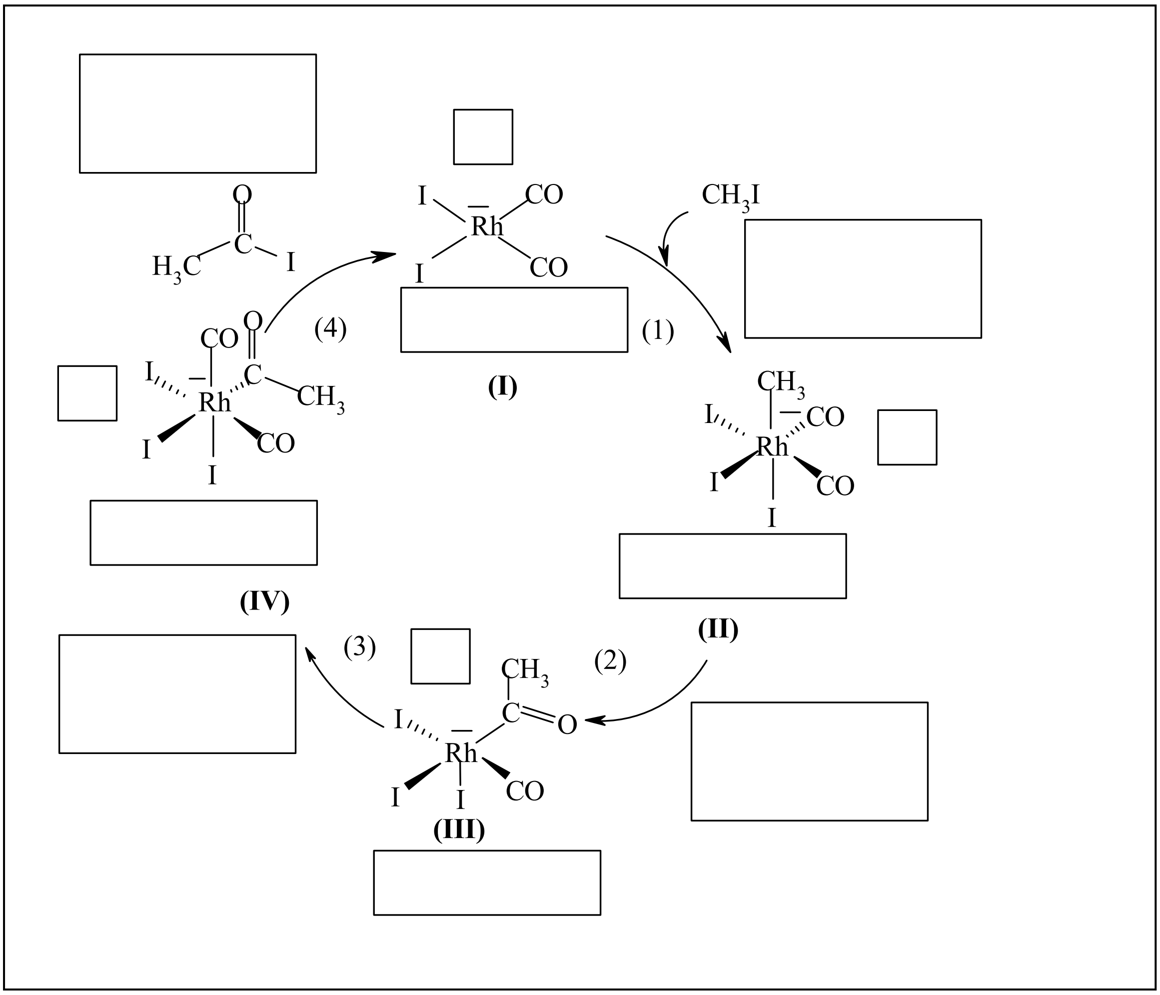
6.6 Write IUPAC names of the following complexes: (i) $[Co(NH_3)_6]Cl_3$
(ii) $K_4[Fe(CN)_6]$ (iii) $Fe(C_5H_5)_2$

(3 marks)

6.7 In most of the organometallic transformations following reactions are known to occur: (a) ligand substitution or dissociation, (b) oxidative addition, (c) reductive elimination, (d) migratory insertion, (e) electrocyclization. Based on these or some more fundamental reactions various catalytic cycles can be proposed. One such cycle for conversion of methanol to acetic acid is indicated below.

$$CH_3OH + CO \xrightarrow{\text{Rh cat. } I^-} CH_3CO_2H \text{ (overall)}$$

The steps in this cycle are labeled as (1), (2), (3), and (4); the intermediate complexes are labeled as I, II, III, and IV. Mark each of these step, with the appropriate letter (a-e) from the above list indicating the nature of that step. Under each intermediate complex write the formal oxidation state and d electron configuration of the central metal (e.g. Mo(II) d4). Place an asterisk beside each co-ordinatively unsaturated ("16-electron") complex



(7 marks)

The following boxes may be used:

☐ To indicate optical activity by *

☐ To indicate metal oxidation state and number of d electrons

☐ To indicate the reaction name from a-e