Indian National Chemistry Olympiad 2015
Theory
(3 hours)

Name: ____

Address for Correspondence: ____

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Pin Code: ☐☐☐☐☐☐ **Tel. No.** (With STD Code**)** ____________________

Mobile No: ______________ **E-mail id:** ____________________

Class: ____________________ **Board:** ____________________

Roll No. ☐☐☐☐ ☐☐☐☐ ☐☐☐☐ **M/F:** ______________

Name of School/Junior College (with Address and Phone Number):

____

____

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: ____________________ **Roll No.** ☐☐☐☐ ☐☐☐☐ ☐☐☐☐

Place: ____________________ **Date:** ______________

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	6	Total
Marks	17	14	26	24	21	12	114
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 **36** pages of problems including answer boxes.
- Total marks for INChO 2015 paper are **114.**
- 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 2nd February 2015.

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
1 cm^{-1}	$= 11.9 \times 10^{-3}\ kJ\ mol^{-1}$
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	$F = 96485\ C\ mol^{-1}$
Temperature	0°C = 273.15 K

Name of Student

Problem 1 **17 marks**

Oxides of nitrogen

Nitrogen is one of the most important elements on earth. It forms several oxides including nitric oxide and nitrogen dioxide. Nitric oxide is an air pollutant produced in the combustion processes in automobile engines and power plants.

1.1 Write the Lewis dot structures of nitric oxide and nitrogen dioxide.

(1mark)

In the chemical industry, nitric oxide is an important intermediate produced by oxidation of ammonia by oxygen. This is the first step in the Ostwald's process of the manufacture of nitric acid.

1.2 Write the balanced equation for the oxidation of ammonia to nitric oxide by oxygen.

(0.5 mark)

1.3 In a closed vessel, at 700 K and a pressure of 1 atm, 100 kmols of ammonia are mixed with 20% excess of air than that required for complete combustion of ammonia. (air contains 80% nitrogen and 20% oxygen on volume basis)

i) Calculate the initial number of moles of oxygen and nitrogen present in the system.

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(1 mark)

ii) At equilibrium, 70% yield of nitric oxide was obtained in the closed vessel. Calculate the mole percent of ammonia and water present in the mixture at equilibrium.

(2 marks)

Some equilibria of nitrogen oxides, which can be exploited commercially are shown below. (**From Questions 1.4 to 1.8, you need to refer to these equations.**)

A) $N_2\,(g) + O_2(g) \rightleftharpoons 2NO(g)$

B) $2NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$

C) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

D) $2NO_2(g) + H_2O(aq) \rightleftharpoons HNO_2(aq) + HNO_3(aq)$

1.4 Using the following data, calculate the standard free energy change in kJ for reaction **A**. The temperature is 298.15 K.

$\Delta H_f°$ of NO(g): 90.37 kJ mol^{-1} S° of N_2(g): 191.5 J mol^{-1}K^{-1}

S°of O_2(g): 205 J mol^{-1}K^{-1} S°of NO(g): 210.6 J mol^{-1}K^{-1}

(1.5 marks)

1.5 At 298.15 K, the ΔG^o of formation for N_2O_4(g), and NO_2(g) are 98.28 kJ mol^{-1} and 51.84 kJ mol^{-1} respectively. Starting with 1 mole of N_2O_4(g) at 1.0 atm and 298.15 K, calculate % of N_2O_4 decomposed if the total pressure is kept constant at 1.0 atm and the temperature maintained at 298.15 K.

(2 marks)

1.6 $\Delta H°$ for the reaction **C** is 58.03 kJ. Assuming $\Delta H°$ to be temperature independent, calculate the temperature at which the fraction of N_2O_4 decomposed is double the value of that calculated in **1.5.**(The pressure is 1 atm)

(2.5 marks)

1.7 The equilibrium represented by **C** was studied at 40°C at a certain pressure. The density of the gaseous mixture was 5.85 g L^{-1}. Calculate the average molecular weight of the gaseous mixture and the degree of dissociation of N_2O_4 at 40°C.

($\Delta G^{\circ} = -1.254$ kJ mol^{-1})

(4 marks)

1.8 Nitric oxide is formed in the combustion of fuel. An internal combustion engine produces 250 ppm (250 mg L^{-1}) of NO (w/v). 100 L of air containing the produced NO was oxidized to NO_2. The NO_2 formed was dissolved in 100 L of water. Calculate the pH of the resulting solution. Refer to reaction **D**. (Given: pK_a of HNO_2 = 3.25)

(2.5 marks)

Name of Student

Problem 2 — 14 marks

Acid Base chemistry

A.

2.1 Vinegar is used in food preparations. The main ingredient of vinegar is acetic acid that gives it a pungent taste. A sample of vinegar has 5% v/v acetic acid. The density of acetic acid is 1.05 g mL^{-1}.

a) Calculate the molarity of acetic acid in vinegar solution.

(1 mark)

b) Calculate the pH of the above vinegar sample. (K_a for acetic acid = 1.75×10^{-5})

(1 mark)

2.2 100 mL of the above vinegar sample is diluted to 250 mL and then 25 mL of the diluted solution is titrated against NaOH solution (0.100 M).

a) Calculate the pH of the solution when 10 mL of NaOH solution was added.

(1.5 marks)

b) Calculate the pH of the solution at the equivalence point (equivalence point is theoretical end point of the titration).

(2 marks)

2.3 A pH meter is usually calibrated using standard buffer solution for which the pH is exactly known. A buffer solution consisting of sodium acetate and acetic acid with pH = 5 is to be used for calibration of a pH meter. How many moles of sodium acetate and acetic acid are required to prepare 250 mL of this buffer solution?

(The total concentration of acetic acid in all forms in the solution is 0. 8 M).

(2 marks)

B.

Two standard methods for estimation of amino acids are described below. In method I, a sample of valine is treated with nitrous acid and the volume of nitrogen gas released is measured. The reaction is as follows:

$(CH_3)_2C(NH_2)COOH + HNO_2 \rightarrow (CH_3)_2C(OH)COOH + N_2 + H_2O$ --------(Method I)

In method II, valine is treated with **excess** of perchloric acid in acetic acid (such a titration is called as a non aqueous titration where glacial acetic acid is used as solvent.)

The reaction is indicated below:

$CH_3CH(NH_2)COOH + HClO_4 \rightarrow CH_3CH(NH_3)^+COOH + ClO_4^-$ ---------(Method II)

After the reaction is complete, the **unreacted** $HClO_4$ is determined by titrating it with standard solution of sodium acetate.

50.0 mL of a 0.150 M solution of $HClO_4$ is added to a sample of valine in glacial acetic acid. The **unreacted** perchloric acid requires 20 mL of 0.180 M solution of sodium acetate.

2.4 Calculate the volume of the nitrogen released (in L) at a pressure of 102658 Pa and a temperature of 298.15°C when the same quantity of sample was used in method I and method II.

(2 marks)

C.

A sample of an aromatic acid weighing 1.743g requires 35 mL of 0.15 M NaOH for complete neutralisation. The vapour of the same acid is found to be 83 times heavier as compared to gaseous hydrogen.

2.5 Calculate the basicity of the aromatic acid.

(1.5 marks)

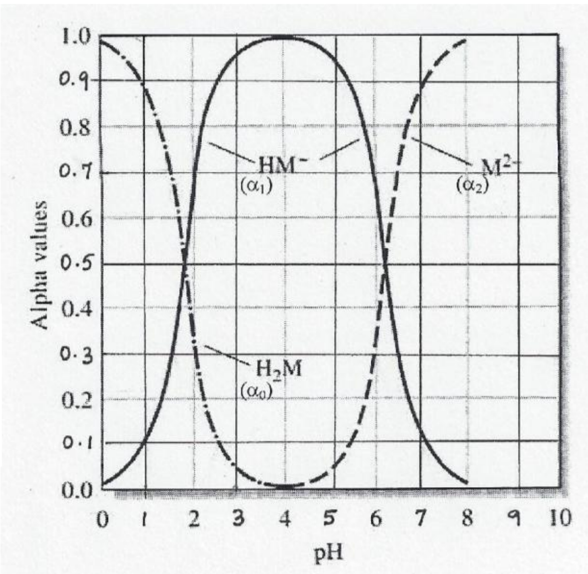
D.

Maleic acid is a diprotic acid. Depending on pH, maleic acid can exist in solution in different forms. If the undissociated acid is represented as H_2M, the different forms in which it can exist in the solution are H_2M, HM^{-1} and M^{-2}.

Let, C_T = Total concentration of acid in all the forms and the fractions (represented as α_n) for different forms of maleic acid can be represented as

$\alpha_0 = [H_2M]/ C_T$ $\alpha_1 = [HM^-]/ C_T$ $\alpha_2 = [M^{-2}]/ C_T$

The following figure indicates variation of fractions of different forms of maleic acid as a function of pH.



Fundamentals of Analytical Chemistry
By Douglas Skoog, Donald West,
F. Holler, Stanley Crouch

2.6 Answer the following questions using the given figure.

a) The pH at which 90% of $[HM^-]$ is converted to $[M^{2-}]$

b) The pKa_1 and pKa_2 of maleic acid are

c) The indicator that can be used for the first equivalence point (**indicate the serial number of the indicator from the given table**)

(3 marks)

No.	Indicator	pH range for change of colour	**No.**	Indicator	pH range for change of colour
1	Phenol red	6.8 – 8.4	**3**	Bromophenol blue	3.0 – 4.6
2	Bromophenol red	5.2 – 6.8	**4**	*m*-cresol purple	1.2 – 2.8

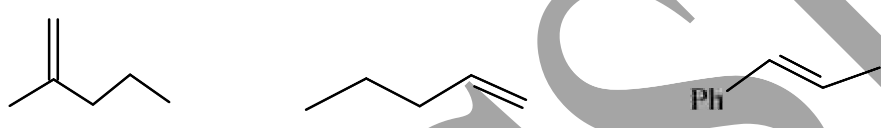
Name of Student

Problem 3 26 marks

Organic Reaction Intermediates

Many organic reactions proceed through intermediates such as carbocations, carbanions, carbon radicals, carbenes etc. The structure and stability of the intermediates are the crucial factors that determine reaction mechanism. For example, in a reaction proceeding through formation of carbocation, the stability of the carbocation determines the rate of the reaction. Hammond postulate is an important tool to discuss transition state. It states that the transition state resembles that side closer to it in free energy.

3.1 Arrange the following olefins in the correct order of rate of addition of HI.



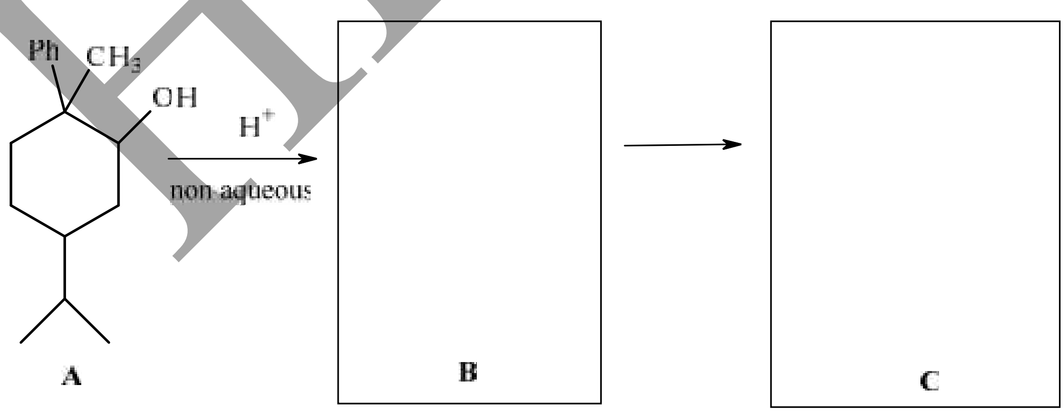
I II III

(1 mark)

Rearrangements of carbocations are very common. The group that migrates is generally the one that is electron rich. Thus sometimes, a product other than the one expected is formed.

Compound **A** on treatment with a Bronsted acid gives compound **C**. In the reaction, **B** is an intermediate formed through a rearrangement.

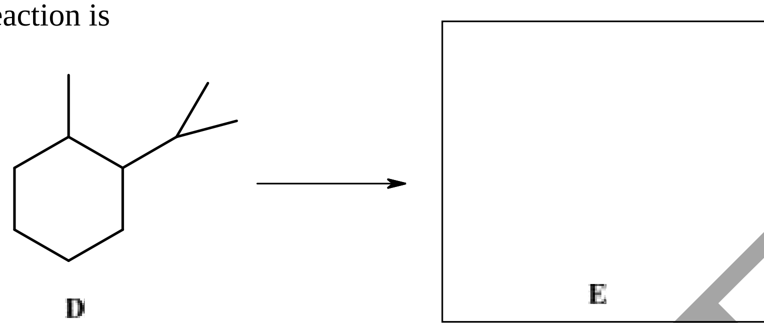
3.2 Identify **B** and **C**.



A

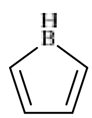
(2 marks)

3.3 Compound **D** on reaction with limited quantity of chlorine in the presence of UV light under ambient conditions gives a mixture of products. The major product **E** of the reaction is

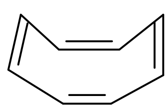


(1 mark)

3.4 Use the following compounds to answer the questions.



1



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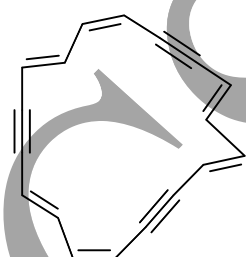

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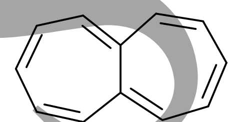

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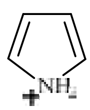

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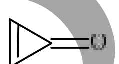

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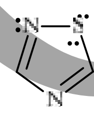

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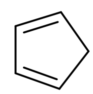

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i) Aromatic compound/s as they are drawn.

ii) Antiaromatic compound/s.

iii) Non aromatic compound/s.

iv) Non aromatic as drawn but has/have resonance structure/s that is/are aromatic.

v) Non aromatic, but has/have aromatic conjugate base.

vi) Non aromatic, and has pKa around (– 3.8)

(5 marks)

Aromatic compounds are difficult to reduce. However, the Australian chemist, A. J. Birch developed a method to reduce aromatic compounds to nonconjugated dienes by treatment with Li/K/Na in liquid ammonia in the presence of an alcohol. The reaction is called Birch reduction. Thus, benzene can be reduced to 1,4-cyclohexadiene. In this reaction the metal gives an electron to the aromatic ring to form a radical anion (an intermediate which is an anion and has an unpaired electron). In this intermediate, the radical centre and anionic centre are at 1,4 positions with respect to each other. Birch (1944) carried out the reduction of 3-methylanisole (3-methylmethoxybenzene) and obtained product **F** which on treatment with hot dilute mineral acid gave **G** ($C_7H_{10}O$).

3.5 Draw the possible structures of **F**.

(1.5 marks)

3.6 Draw the possible stable structures of **G** based on the structures of **F**.

(2.5 marks)

G that is actually obtained, is not chiral. On reaction with Br_2, it gave compound **H** which on heating with alcoholic KOH gave **I** (C_7H_9BrO).

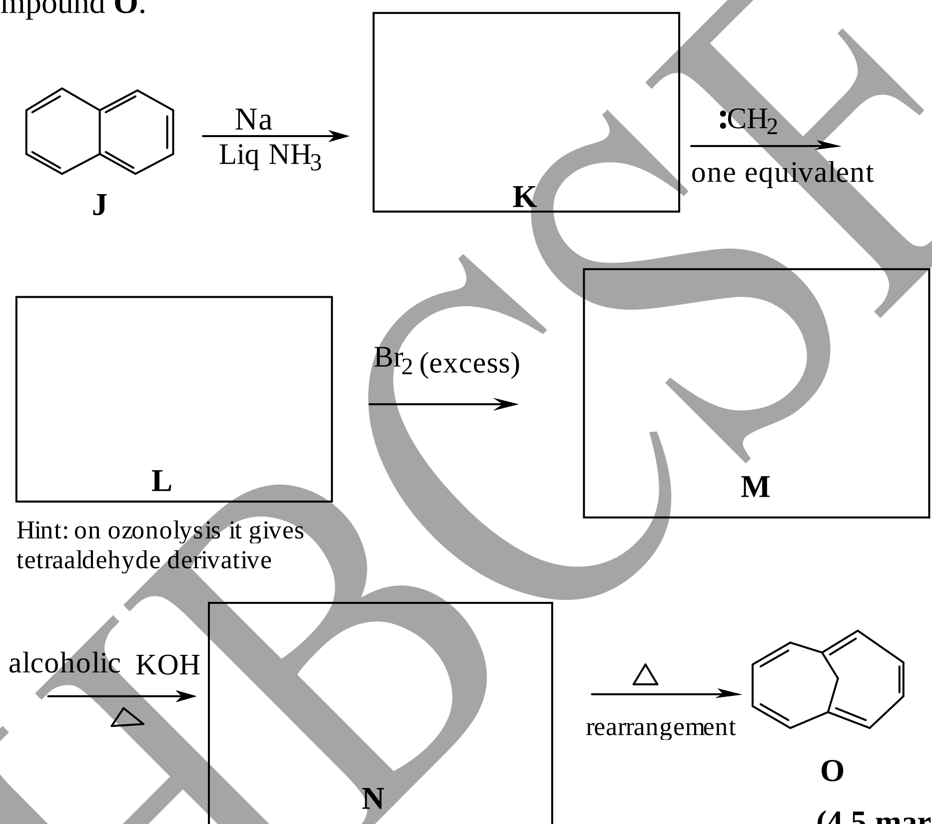
3.7 Identify **G**, **H** and **I**.

G **H** **I**

(2 marks)

E. Vogel is well known for his work on bridged annulenes. Annulenes are large ring compounds containing continuous conjugation. Compound **O** is one such compound which is synthesized from naphthalene (**J**) by the following route. Compound **K** adds three equivalents of bromine. Carbene ($:CH_2$) is a very reactive intermediate. It reacts with an olefinic double bond to form cyclopropane.

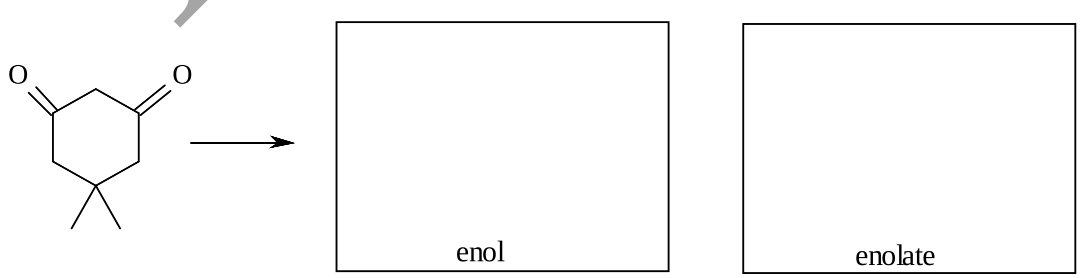
3.9 Draw the missing structures in the following sequence of reactions for the synthesis of compound **O**.



(4.5 marks)

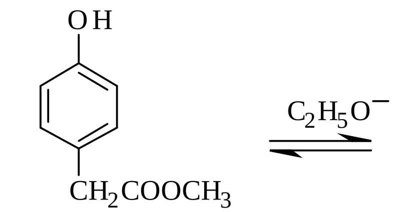
Carbonyl compounds with acidic hydrogen can exhibit tautomerism and can exist in the enol form. The conjugate base of enol is called as enolate.

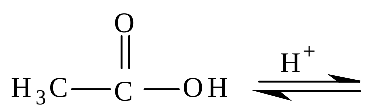
3.10 i) Draw the most stable enol and the corresponding enolate of the following compound.



(1 mark)

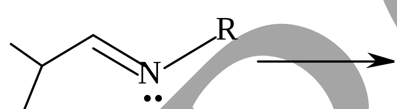
ii) Draw the structures of the most favorable products obtained from the reactants in the following reactions

a) 

b) 

(1 mark)

3.11 Aza-enolates are the nitrogen analogues of enolates. Draw the structure of the aza-enolate of the following .



(1 mark)

3.12 The reactant shown in **3.11** can be prepared by the condensation of

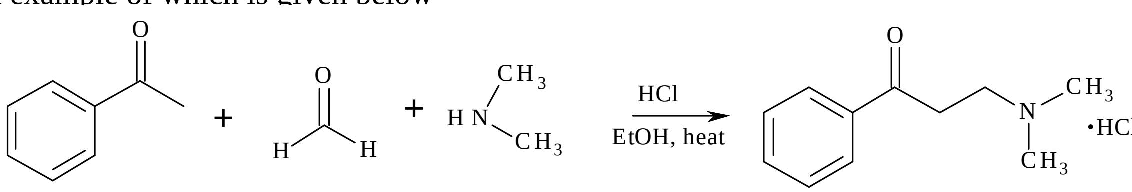
i) An aldehyde and a secondary amine ☐

ii) A ketone and a secondary amine ☐

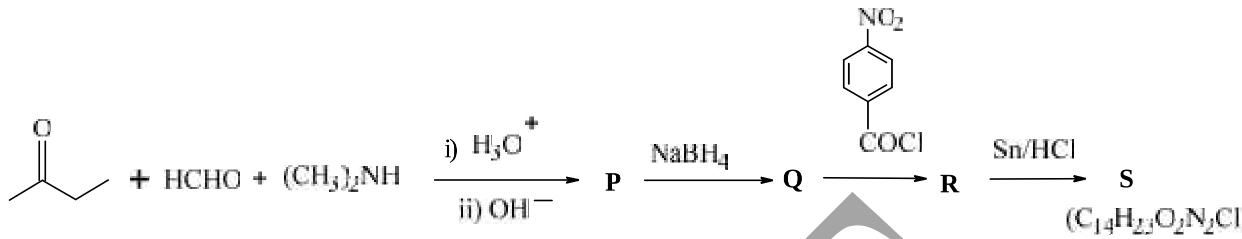
iii) An aldehyde and a primary amine ☐

iv) A ketone and a primary amine ☐ **(1 mark)**

A Mannich reaction is a reaction between formaldehyde, a secondary amine and a ketone, an example of which is given below



3.13 Identify the structures of compounds **P** $\rightarrow$ **S** in the synthesis of a local anaesthetic, Tutocaine hydrochloride (**S**). The first step in this synthesis involves a Mannich reaction.



P	Q	R	S

(2.5 marks)

Name of Student

Problem 4 24 marks

Chemistry of Potassium Permanganate

Potassium Permanganate ($KMnO_4$); chameleon mineral or Condy's crystals is an inorganic compound which dissolves in water to give an intensely pink or purple solution. The evaporation of this solution leaves prismatic purplish-black glistening crystals.

On a small scale potassium permanganate is prepared from the disproportionation of potassium manganate in acidic medium.

4.1 Write a balanced equation for this reaction.

(1mark)

4.2 Draw the Lewis dot structures of manganate and permanganate species. State which of the species is paramagnetic. Calculate the spin only magnetic moment for the paramagnetic species.

Permanganate manganate

(2.5 marks)

4.3 When concentrated H_2SO_4 is added to $KMnO_4$ it gives a greenish oily dimanganese heptaoxide.

a) Write the balanced equation for this reaction.

(1mark)

b) Draw the structure of dimanganese heptaoxide.

(1 mark)

4.5 On standing, the above oxide decomposes to form manganese dioxide. Write a balanced chemical equation for the reaction.

(0.5 mark)

The Latimer Diagram for a series of manganese species in acidic medium (pH = 1) is given below. The emf values (E°) shown are standard reduction potentials in volts.

$$MnO_4^- \xrightarrow{E_1^\circ = 0.90} HMnO_4^- \xrightarrow{E_2^\circ = 2.09} MnO_2 \xrightarrow{E_3^\circ = 0.95} Mn^{3+} \xrightarrow{E_4^\circ = 1.51} Mn^{2+} \xrightarrow{E_5^\circ = -1.18} Mn$$

4.6 In acidic medium, solid MnO_2 is converted to Mn^{2+} and MnO_4^-.

i) Write balanced equations for the half cell reactions involved and the overall reaction.

At cathode:

At anode:

Overall:

(1.5 marks)

ii) Using the Latimer diagram, calculate the standard electrode potential for each half cell reaction and for the overall cell reaction.

(3 marks)

iii) Calculate K for the overall reaction.

(1mark)

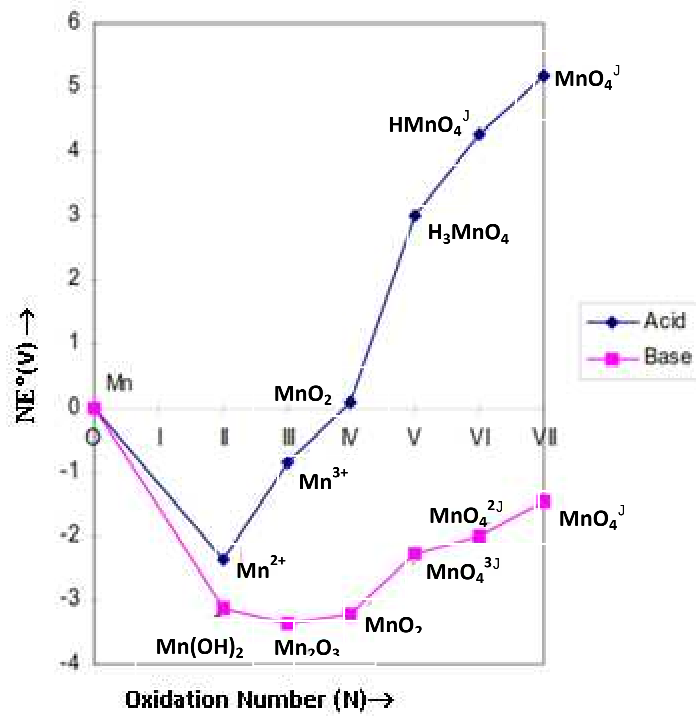
In an acidic medium MnO_4^- is a strong oxidizing agent and is thus often used in redox titration.

Medical shops sell 6% (w/w) aqueous solution of H_2O_2 as a disinfectant. X g of this H_2O_2 solution was titrated using $KMnO_4$ (0.02 M) solution in an acidic medium. The sample required 15.0 mL $KMnO_4$ solution.

4.7 Write balanced equation for the reaction involved in the titration. Calculate the amount of H_2O_2 in grams that was titrated. (Show the relevant steps).

(3 marks)

The Frost Diagram (also known as oxidation state diagram) of an element (X) is a plot of volt-equivalent (NE°) for a couple X(N)/X(0) against oxidation number (N) of the element. Such a plot can be constructed from Latimer diagram. The Frost diagram for manganese species in acidic and basic condition is given below.



Ref: http://classes.uleth.ca/200501/chem2810a/lecture_20.pdf

4.8 Using the given diagram fill in the blanks.

i) The slope of the line joining two successive points is equal to ________ of the relevant couple.

ii) The most stable oxidation state of manganese in acidic condition is ________ and in basic condition is ________

iii) In basic condition, the species of manganese that will disproportionate is ________

iv) In acidic condition, the **two pairs** of manganese species that will comproportionate (opposite of disproportionation) are ________ ________

v) In basic condition, the manganese specie/s that will act as reducing agents are/is

vi) In basic condition, the weakest oxidizing agent is

(4.5 marks)

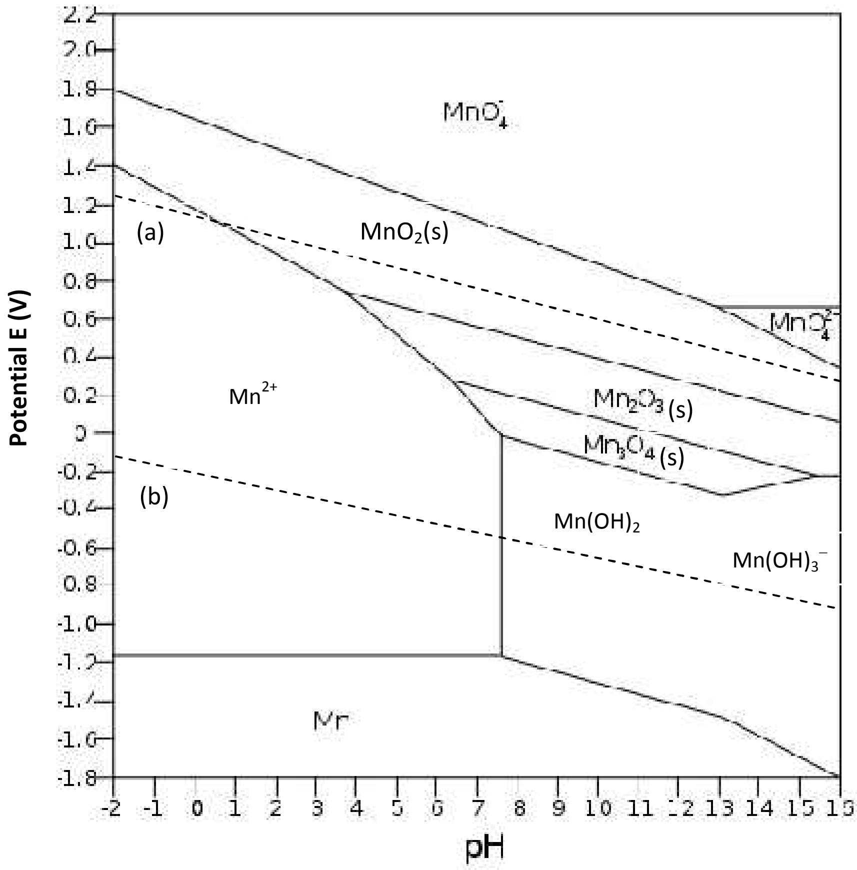
Pourbaix diagram of manganese is the plot of the potential (E) vs pH and indicates the conditions under which different species of manganese are stable in aqueous medium at 25°C and 1M concentration. Such diagrams are used frequently in geochemical, environmental and corrosion studies. In this diagram,

1) Horizontal line separates species related by electron transfer only.

2) Vertical lines separate species related by proton transfer.

3) Slanting lines separate species related by both proton and electron transfer.

Between the dashed line (**a**) and (**b**) water is stable, whereas above line (**a**) it is oxidized to O_2 and below line (**b)** it decomposes to H_2.



(Ref: http://commons.wikimedia.org/wiki/File:Pourbaix_diagram_for_Manganese.svg)

4.9 Based on the Pourbaix diagram of manganese given above, answer the following questions.

i) Which specie/s of manganese is predominant in

a) oxygen rich lakes of pH ≈ 7 [ ]

b) highly oxygen depleted lakes that are contaminated with bases (pH ≈ 10)?

[ ]

ii) It is observed that clear well water, that is slightly acidic (pH ≈ 6) deposits solid/s on standing in toilet bowls.

a) The solid/s species is/are [ ]

b) The manganese species that is found dissolved in well water while it is still underground is [ ]

iii) Identify the specie/s that exist/s in ocean water at pH = 8 and E = + 0.2V to + 0.6 V.

[ ]

(5 marks)

Name of Student

Problem 5 21 marks

Natural Nitrogen Compounds

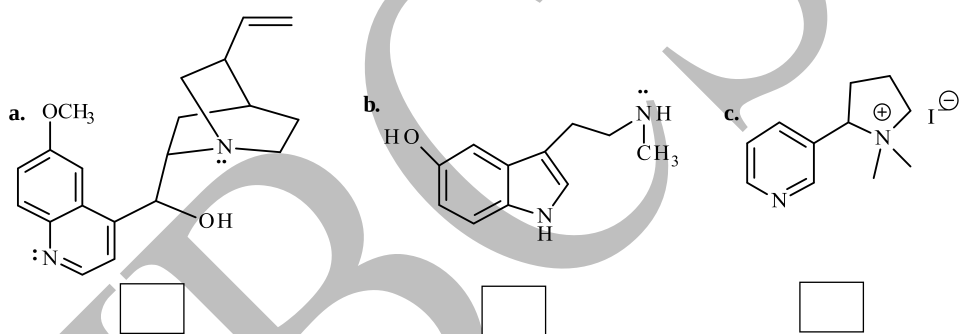
A variety of nitrogen compounds are found in both plant and animal kingdoms. Nitrogen is present in several classes of natural products like alkaloids, nucleic acids, vitamins etc and these compounds have physiological effects.

A stereogenic center is an atom, bearing groups, such that an interchange of any two groups leads to a stereoisomer. Nitrogen containing compounds can also be chiral and exhibit optical activity.

5.1 Some compounds are given below. Label them as

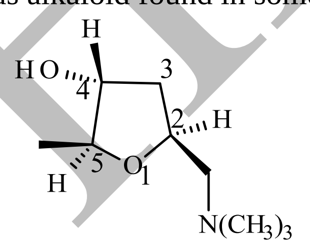
I. Achiral **II.** Chiral; enantiomers cannot be separated

III. Chiral; enantiomers can be separated.



(1.5 marks)

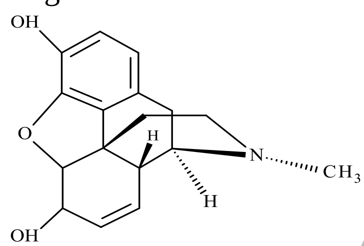
Alkaloids are basic nitrogeneous compounds of plant origin. (+) - Muscarine is a poisonous alkaloid found in some mushrooms.



5.2 Draw the enantiomer of (+) −Muscarine and give its stereodescriptors.

(2 marks)

Several alkaloids occur in opium which is a narcotic drug. Morphine is one of them. It is an analgesic and is used to relieve intense pain.



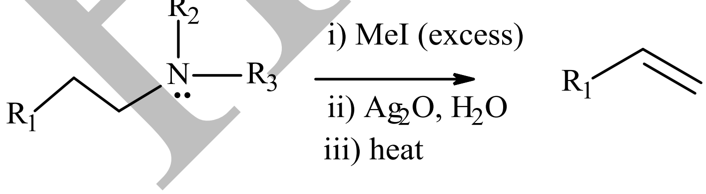
Morphine

5.3 How many stereogenic centres are present in Morphine?

a) 3 ☐ b) 4 ☐ c) 5 ☐ d) 6 ☐

(1 mark)

The Hofmann exhaustive methylation is a method used in structure determination of alkaloids. The reaction involves quarternization of the nitrogen followed by elimination to yield an alkene as one of the products. It is schematically represented below.



The diacetyl derivative of morphine is heroin, which is also a narcotic drug.

Heroin is subjected to Hofmann exhaustive methylation to eliminate nitrogen completely to obtain product **A**.

5.4 The number of moles of methyl iodide required for complete removal of nitrogen from heroin is

a) 1 ☐ b) 2 ☐ c) 3 ☐ d) 4 ☐

(1 mark)

5.5 Draw the structure of '**A**'.

A

(2 marks)

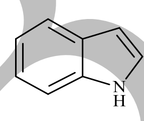
'**A**' is treated with an excess of bromine.

5.6 The number of molecules of bromine consumed by one molecule of '**A**' is

a) 2 ☐ b) 3 ☐ c) 4 ☐ d) 5 ☐

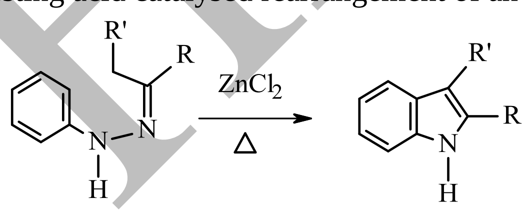
(1 mark)

Another interesting class of nitrogen containing alkaloids is the Indole alkaloids that contain the indole ring.



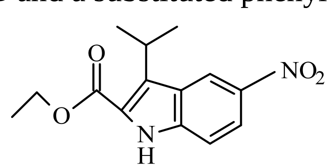
Indole

Indole and its derivatives are synthesized by the Fischer indole synthesis, that involves an interesting acid catalysed rearrangement of an arylhydrazone as represented below.



aryl hydrazone

The following indole derivative was synthesized by the Fischer synthesis using a carbonyl compound **B** and a substituted phenyl hydrazine derivative **C**.



5.7 Draw the structures for **B** and **C**.

B **C**

(1.5 marks)

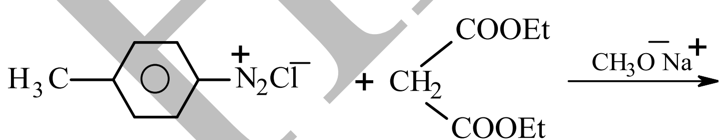
Arene diazonium salts are important intermediates that can be directly reduced to aryl hydrazines or can be used to prepare aryl hydrazones. They are also used to prepare azo dyes, in which case they function as electrophiles.

5.8 Draw the most important resonance structures of benzene diazonium ion.

(1 mark)

Arene diazonium salts couple with aliphatic compounds containing acidic carbon atom (active methylene compounds) to form azo derivatives. The initial azo compound tautomerises to the hydrazo derivative. If a given compound does not permit such a tautomerism, the compound may lose a suitable group from the coupling site to allow for the tautomerism.

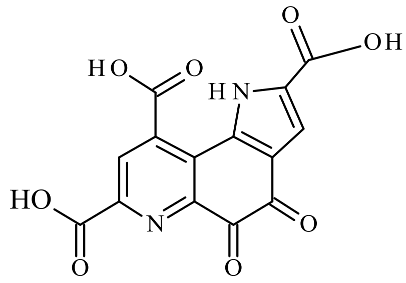
5.9 Complete the following reaction



azo compound

(1 mark)

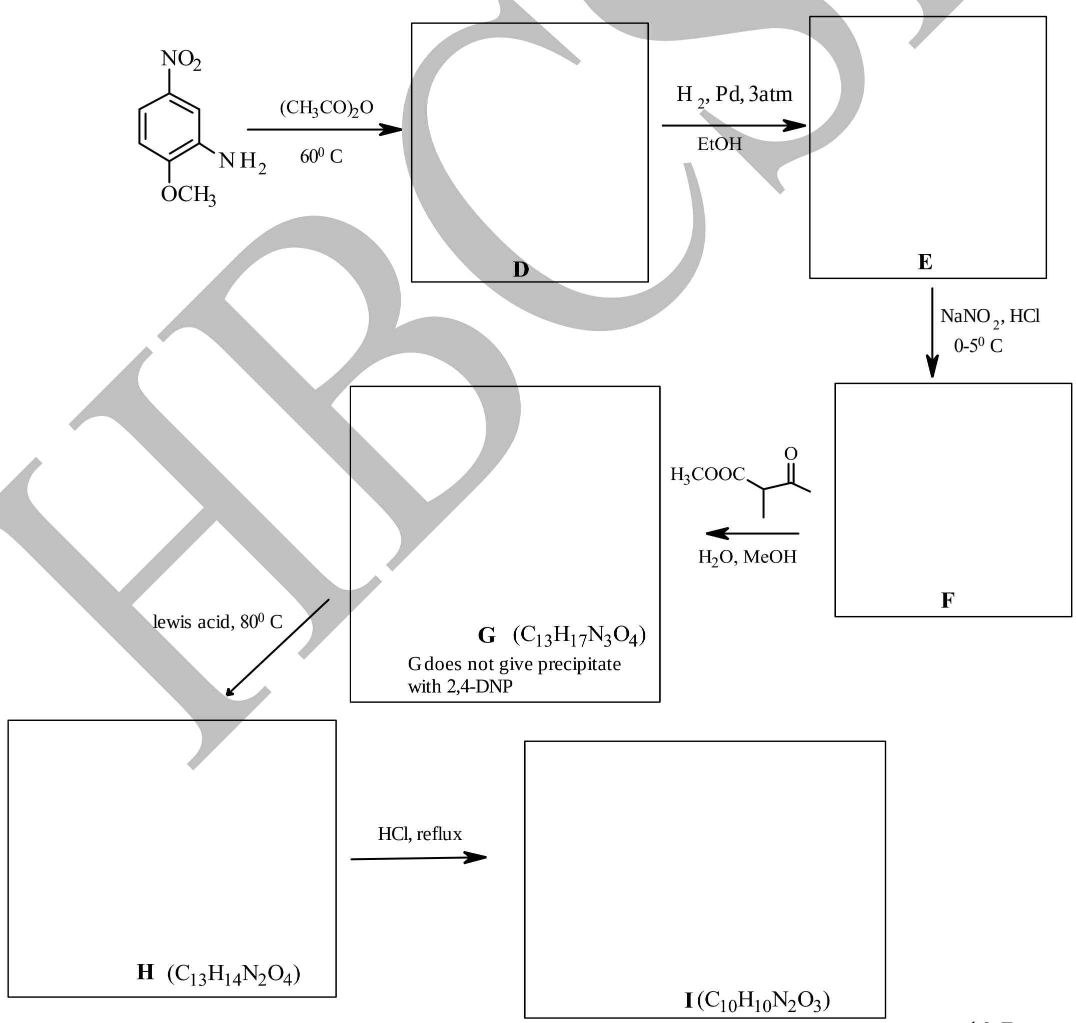
Compound **'J'** is an alkaloid and a redox cofactor for the enzyme *alcohol dehydrogenase* and plays a critical role in cell signaling pathways.



J

Compound '**I**' is a key intermediate in the synthesis of '**J**'. This synthesis path involves the formation of a hydrazone.

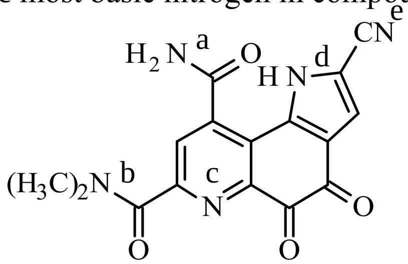
5.10 Complete the synthesis of compound **'I'** by drawing the missing structures in the boxes below.



(4.5 marks)

Compound '**K**' a precursor of **'J'** can be obtained from **I**.

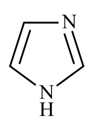
5.11 The most basic nitrogen in compound '**K**' is



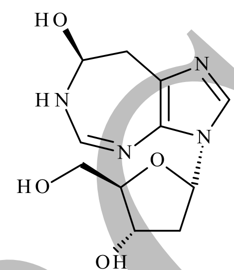
K

(0.5 mark)

Natural compounds containing the imidazole ring have been found to be physiologically active. Hence efforts have been made to synthesise such compounds. One such synthetic drug is Pentostatin, which is used as an antiviral and antitumour agent. A key intermediate in the synthesis of Pentostatin is compound '**O**' ($C_{12}H_{10}N_4O_5$)

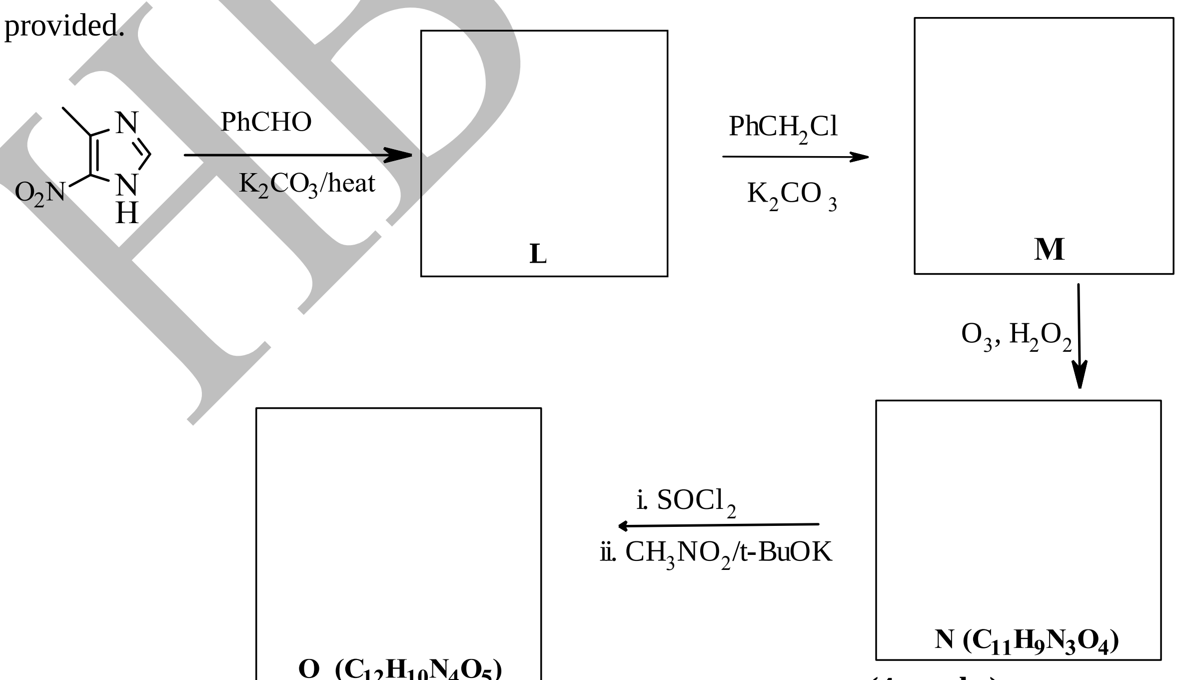


Imidazole



Pentostatin

5.12 Complete the synthesis of compound **'O'** by drawing the missing structures in the boxes provided.



(4 marks)

Name of Student

Problem 6 **12 marks**

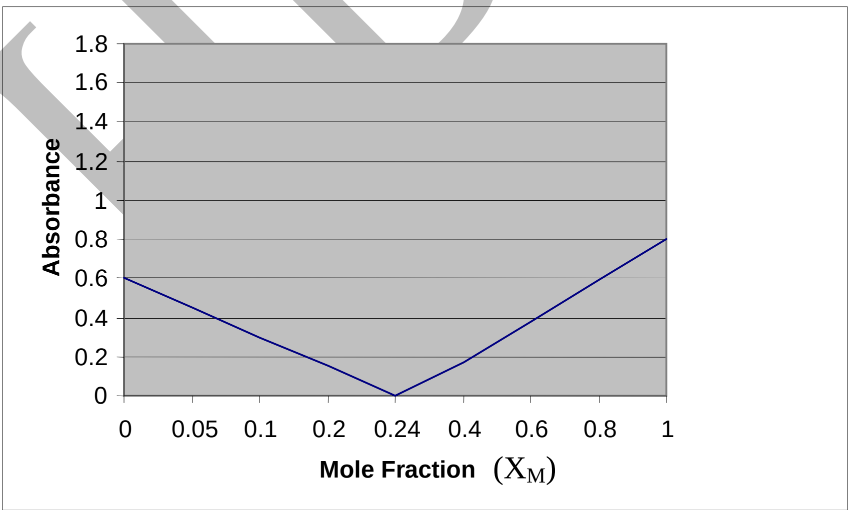
Beer-Lambert Law

A.

Beer–Lambert law deals with the relationship between the extent of absorption of radiation by a species and its concentration. The law states that 'absorbance (A) is directly proportional to concentration (expressed as mol L^{-1}) at any given wavelength for a dilute solution. Mathematically it can be expressed as A **=** ε *l* c, where, ε = molar absorptivity (units = L cm^{-1} mol^{-1}), *l* = path length in cm, A = $-\log_{10}(I/I_o)$, where I_o = intensity of the incident radiation and I = intensity of the transmitted radiation. The ratio of (I / I_o) is called as transmittance (T).

Method of continuous variation is one of the standard methods used for the spectrophotometric determination of the composition of a complex between a metal **M** and a ligand **L**. In this method, the sum of the molar concentrations of the metal **M** and the ligand **L** is kept constant, but their relative ratio is varied. The following graph is obtained for one such analysis. **Use the graph** to answer the questions from **6.1** to **6.4**.

($X_M = C_M / (C_M + C_L)$), where C_M = concentration of the metal ion in all forms, C_L = concentration of ligand in all forms).



6.1 Deduce by calculations the species that absorb when $X_M = 0$ and $X_M = 1$ respectively.

(1 mark)

6.2 What is the ratio of the molar absorptivities of **M** and **L**?

(2 marks)

6.3 What percentage of the incident light is transmitted through solutions when (i) $X_M = 0.1$ and when (ii) $X_L = 0.2$?

(1.5 marks)

6.4 Determine the composition of the complex formed. Show your calculations.

(2 marks)

B.

6.5 For practical purpose**,** the preferred percentage transmittance range for spectrophotometric measurement should be between 20% to 65% (as the error in the measurement in this range is minimum). In an experiment which involved the determination of absorbance for a co-ordination complex of iron (ε = 12000), calculate the concentrations of the complex corresponding to the above transmittance range.

(1.5 marks)

The chelate $CuQ_2^{2-}{}_{(aq)}$ formed by $Cu^{2+}{}_{(aq)}$ and the complexing agent $Q^{2-}{}_{(aq)}$ absorbs at 480 nm. When the concentration of chelating agent $Q^{2-}{}_{(aq)}$ is five times in excess as compared to $Cu^{2+}{}_{(aq)}$, the absorbance of the chelate solution depends only on molar concentration of $Cu^{2+}{}_{(aq)}$ and obeys Beer-Lambert law. Neither $Cu^{2+}{}_{(aq)}$ nor $Q^{2-}{}_{(aq)}$ absorbs at 480 nm. A solution that contains 3.30 x 10^{-4} M Cu^{2+} and 8.60 x 10^{-3} M of Q^{2-} has absorbance 0.690 at λ = 480 nm.

Another solution that was prepared by mixing 3.30 x 10^{-4} M of Cu^{2+} and 6.500 x 10^{-4} M of Q^{2-} was found to have absorbance 0.610 at the same wavelength. (cell length l = 1 cm).

6.6 From the given data, calculate the equilibrium constant (called as formation constant K_f) for the following process

$Cu^{2+}{}_{(aq)} + 2Q^{2-}{}_{(aq)} \rightleftharpoons CuQ_2^{2-}{}_{(aq)}$.

(4 marks)

Rough Page

Rough Page

Rough Page

Rough Page

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	9 VIII 8	10	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

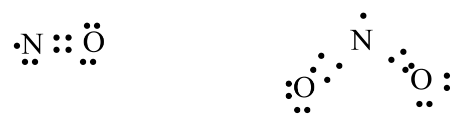
Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm 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]

Tentative Solutions

Problem 1 — 17 marks

Oxides of nitrogen

1.1



(1mark)

1.2 $2NH_3\,(g) + 2.5\,O_2\,(g) \rightleftharpoons 2\,NO\,(g) + 3H_2O\,(g)$ **(0.5 mark)**

1.3 i) 600 k moles of N_2 **(1 mark)**

ii) ammonia = 3.4%, water = 12.10% **(2 marks)**

1.4 ΔG° = 173.37 kJ **(1.5 marks)**

1.5 15.45 % will decompose. **(2 marks)**

1.6 T = 315.93 K **(2.5 marks)**

1.7 α = 0.39 and M_{av} = 66.19 **(4 marks)**

1.8 pH = 2.38 **(2.5 marks)**

Problem 2 **14 marks**

Acid Base chemistry

A.

2.1 a) Molarity = 0.875 M **(1 mark)**

b) pH= 2.41 **(1 mark)**

2.2 a) pH = 3.87 **(1.5 marks)**

b) pH = 8.32 **(2 marks)**

2.3 moles of salt required = 0.128 mole

moles of acid required = 0.0719 mole **(2 marks)**

B.

2.4 $V(N_2)$ = 0.094 L **(2 marks)**

C.

2.5 y = 2 Thus acid is dibasic **(1.5 marks)**

D.

2.6 Answer the following questions using the given figure.

a) 7

b) 1.9 and 6.2

c) 3 **(3 marks)**

Problem 3 26 marks

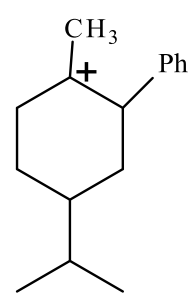
Organic Reaction Intermediates

3.1

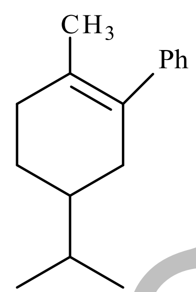
III > I > II

(1 mark)

3.2



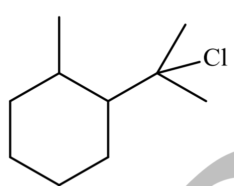
B



C

(2 marks)

3.3



E

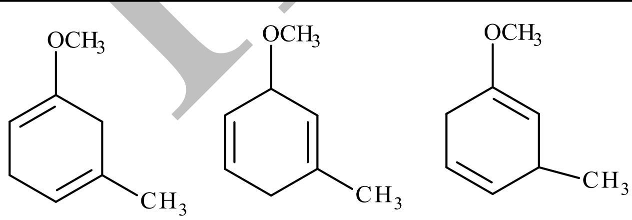
(1 mark)

3.4

i)	**3,7**	iv)	**6**
ii)	**1,4**	v)	**8 and 5**
iii)	**2, 5**	vi)	**5**

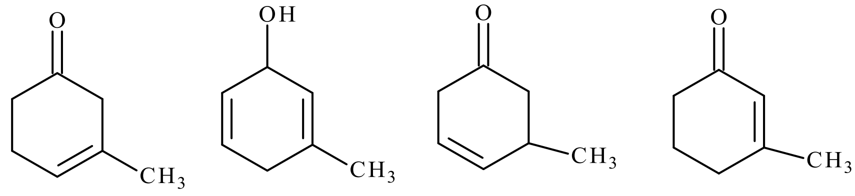
(5 marks)

3.5



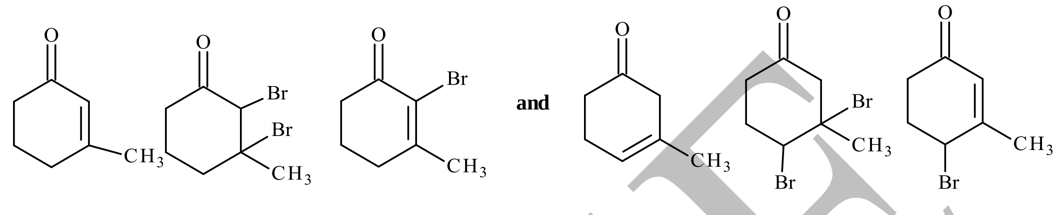
(1.5 marks)

3.6



(2.5 marks)

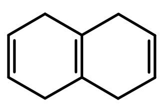
3.7



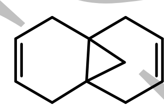
G **H** **I** **G** **H** **I**

(2 marks)

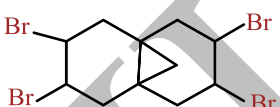
3.9



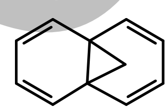
K



L



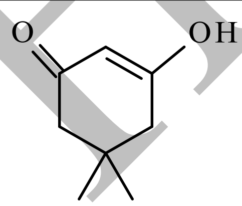
M



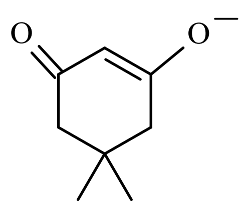
N

(4.5 marks)

3.10 i)



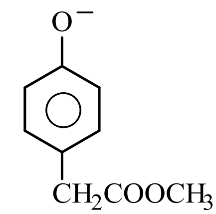
enol



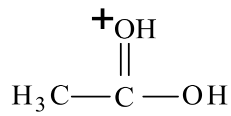
enolate

(1 mark)

ii) a)

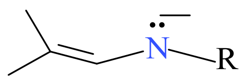


b)



(1 mark)

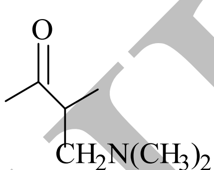
3.11



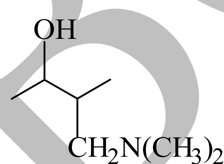
(1 mark)

3.12 iii) An aldehyde and a primary amine X **(1 mark)**

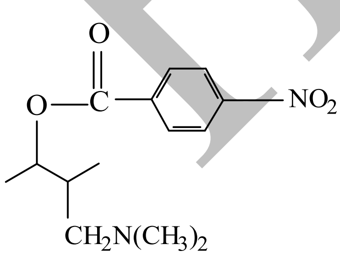
3.13



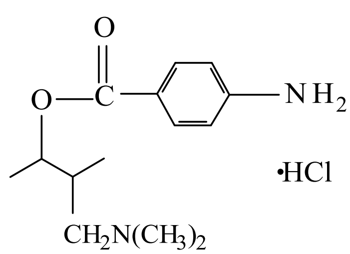
P



Q



R



S

(2.5 marks)

Problem 4 — 24 marks

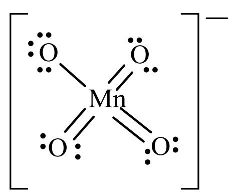
Chemistry of Potassium Permanganate

4.1

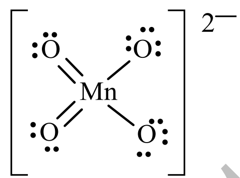
$3MnO_4^{2-}(aq) + 4H^+ (aq) \rightarrow 2MnO_4^-(aq) + MnO_2 (s) + 2H_2O$

(1mark)

4.2



MnO_4^-



MnO_4^{2-}

B.M = $\sqrt{n(n+2)}$ =1.73 B.M → MnO_4^{2-} (n=1)

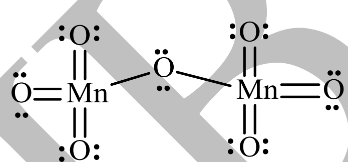
(2.5 marks)

4.3 a)

$2H_2SO_4 + 2KMnO_4 \rightarrow Mn_2O_7 + 2KHSO_4 + H_2O$

(1mark)

b)



Mn_2O_7

(1 mark)

4.5

$2\ Mn_2O_7 \rightarrow 4MnO_2\ (s) + 3O_2\ (g)$

(0.5 mark)

4.6 i)

At cathode:

$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{+2} + 2H_2O$………(1)

At Anode:

$MnO_2(s) + 2H_2O \rightarrow MnO_4^- + 4H^+ + 3e^-$………(2)

Overall

$5MnO_2 + 4H^+ \rightarrow 3Mn^{+2} + 2MnO_4^- + 2H_2O$………(3)

(1.5 marks)

ii)

$$E_{cathode} = 1.230\ V$$
$$E_{anode} = 1.693\ V$$
$$E_{overall} = -0.463\ V$$

(3 marks)

iii) $K = 1.09 \times 10^{-47}$

(1mark)

4.7 0.425g of sample of 6% H_2O_2 was weighed. **(3 marks)**

4.8 i) E°

ii) Mn^{2+} | Mn_2O_3

iii) MnO_4^{3-}

iv) Mn and MnO_2 | Mn^{3+} and H_3MnO_4

v) Mn^0 and $Mn(OH)_2$

vi) MnO_2

(4.5 marks)

4.9 i) a) MnO_2 and MnO_4^- b) $Mn(OH)_2$ and Mn

ii) a) MnO_2 and Mn_2O_3 b) Mn^{2+}

iii) Mn_2O_3 and Mn_3O_4

(5 marks)

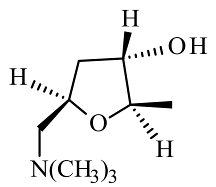
Problem 5 — 21 marks

Natural Nitrogen Compounds

5.1 a. III b. II c. III

(1.5 marks)

5.2



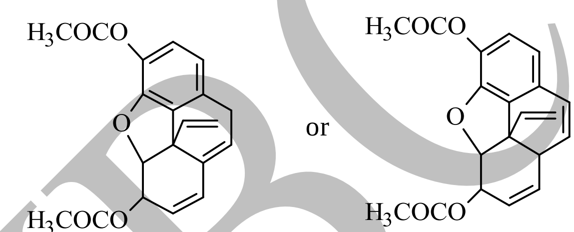
2R, 4S, 5R

(2 marks)

5.3 d) 6 X (1 mark)

5.4 b) 2 X (1 mark)

5.5

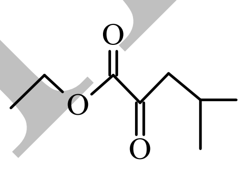


A

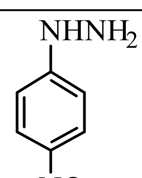
(2 marks)

5.6 b) 3 X (1 mark)

5.7



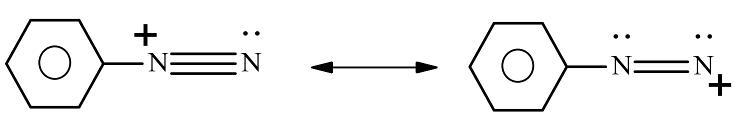
B



C

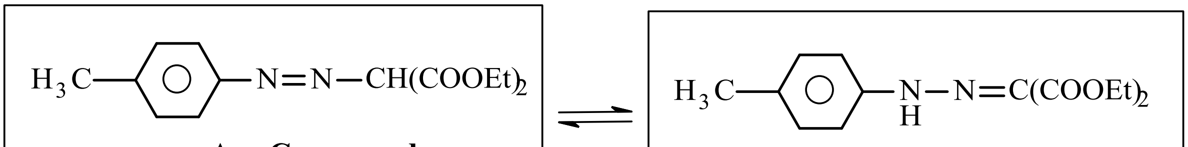
(1.5 marks)

5.8



(1 mark)

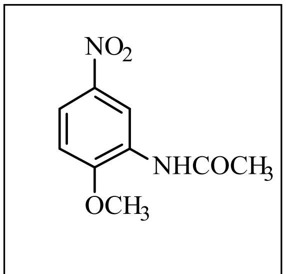
5.9



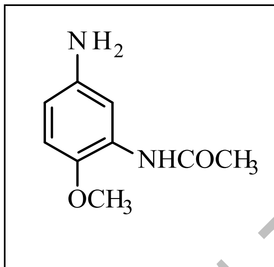
Azo Compound

(1 mark)

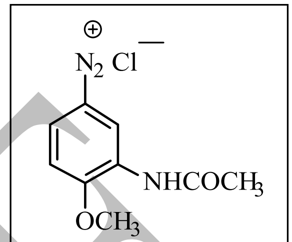
5.10



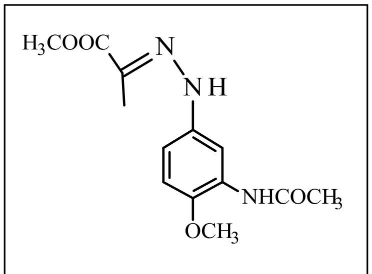
D



E

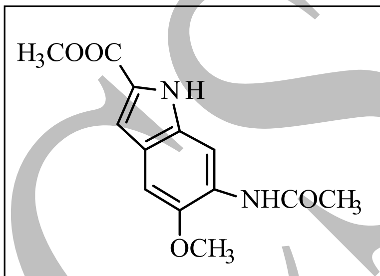


F

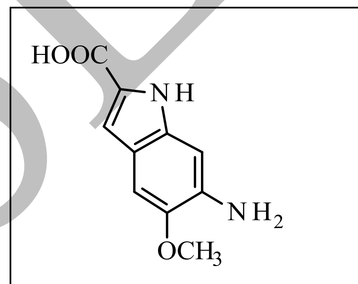


G ($C_{13}H_{17}N_3O_4$)

G does not give precipitate with 2,4-DNP



H ($C_{13}H_{14}N_2O_4$)

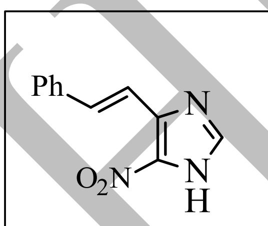


I ($C_{10}H_{10}N_2O_3$)

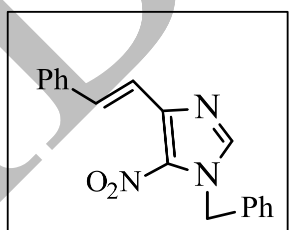
(4.5 marks)

5.11 **C** **(0.5 mark)**

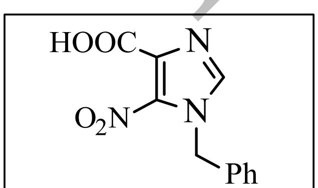
5.12



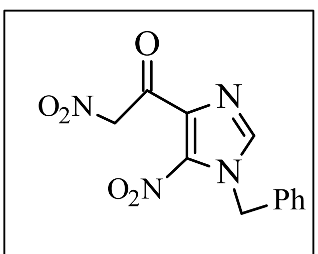
L



M



N ($C_{11}H_9N_3O_4$)



O ($C_{12}H_{10}N_4O_5$)

(4 marks)

Problem 6 12 marks

Beer-Lambert Law

A.

6.1

L absorbs at $X_M = 0$ M absorbs at $X_M = 1$

(1 mark)

6.2

$\varepsilon_M = 1.33\ \varepsilon_L$

(2 marks)

6.3 What percentage of the incident light is transmitted through solutions when (i) $X_M = 0.1$ and when (ii) $X_L = 0.2$?

For $X_M = 0.1$: 50% has been transmitted

For $X_L = 0.2$: 25.1% has been transmitted

(1.5 marks)

6.4

The composition of the complex is ML_3

(2 marks)

B.

6.5

$C_1 = 5.825 \times 10^{-5}\,M$

$C_2 = 1.56 \times 10^{-5}\,M$

(1.5 marks)

6.6

$K_f = 1.764 \times 10^{9}$

(4 marks)