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## Problem 1

21 marks

## Bombykol – An insect pheromone

Pheromones are compounds secreted by animals for intra species communication. Synthetic pheromones can therefore be used as environment-friendly chemicals for pest control. The first insect pheromone, whose structure was elucidated by Butenandt in 1959, was Bombykol, the female-produced silkworm moth sex attractant.

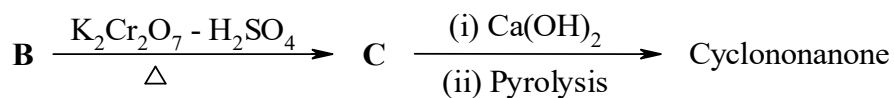
Ozonolysis is a standard method of structure determination. Bombykol ( $C_{16}H_{30}O$ ) undergoes ozonolysis as shown below –



- 1.1 Compound A on heating with dilute NaOH gives 2-ethyl-2-hexenal. Draw the structure of compound A.

(1 mark)

Cyclononanone is obtained from compound B ( $C_{10}H_{20}O_2$ ) as follows –



- 1.2 The structures of compound B and C are:

**B**

**C**

(1 mark)

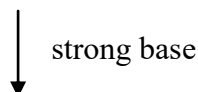
1.3 Draw the structure of Bombykol.

(1 mark)

A method for the synthesis of Bombykol involves a Wittig reaction. Georg Wittig, a German chemist, received the Nobel Prize (1979) for demonstrating the synthetic potential of organophosphorus compounds.

1.4 An alkyl halide, RX, reacts with  $\text{PPh}_3$  to form a salt, which on reaction with a strong base gives a neutral organophosphorus compound, called the Wittig reagent. Complete the following reactions (a and b) in which two Wittig reagents **D** and **E** are formed.

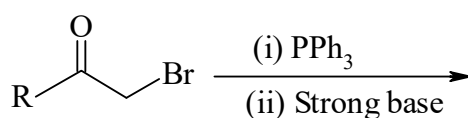
(a) 1-bromopropane +  $\text{PPh}_3$



**D**

(1 mark)

(b)



**E**

(1 mark)

Draw the resonance structures of **E**.

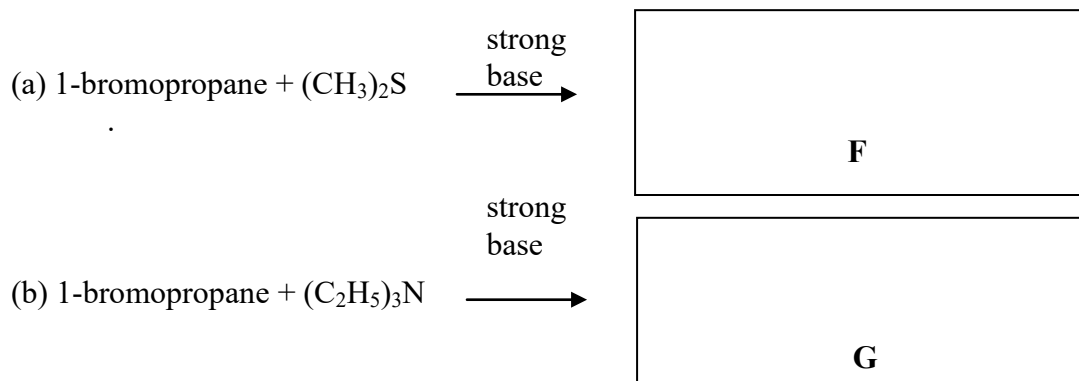
(1 mark)

1.5 The characteristic bonding in a Wittig reagent involves the following orbital overlap:

- (a)  $p\pi - p\pi$
- (b)  $p\pi - d\pi$
- (c)  $d\pi - d\pi$
- (d)  $\pi - \sigma$

(1 mark)

1.6 Draw the structures of the following compounds **F** and **G** which are analogous to Wittig reagents.

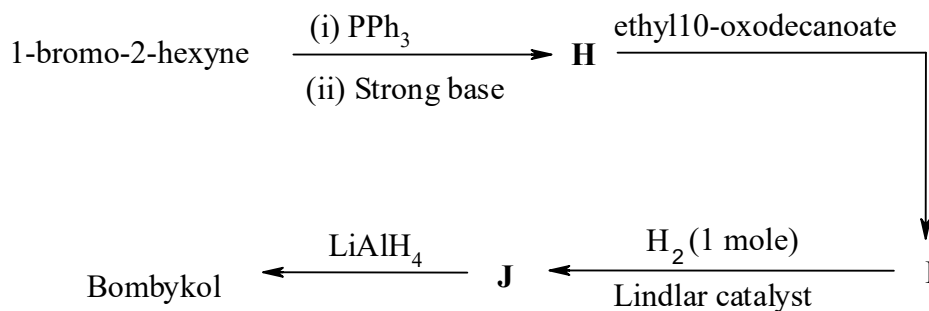


(1 mark)

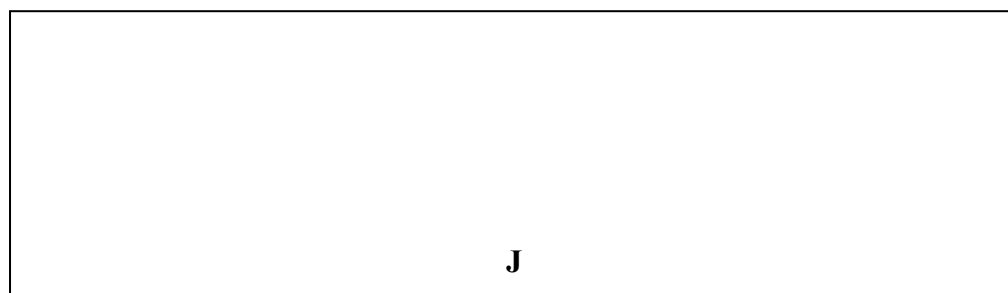
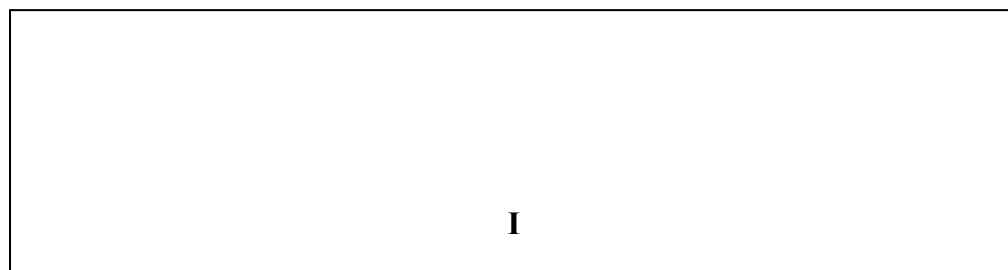
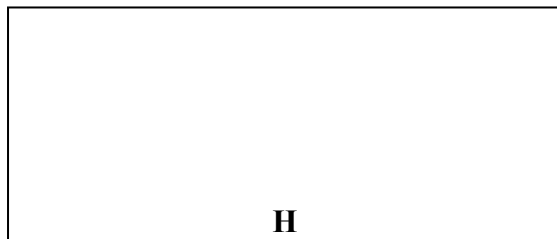
1.7 Out of the three analogous compounds, **D**, **F** and **G**, the least stable one is

(1 mark)

1.8 Wittig reagents react with aldehydes/ketones to give olefins. A resonance stabilized Wittig reagent leads to the *trans* product. Bombykol is synthesized via a Wittig reaction as follows –

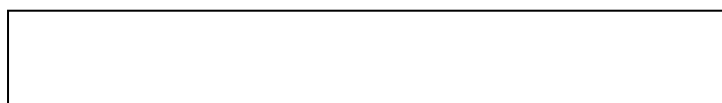


Draw structures of compounds **H**, **I**, and **J**, indicating stereochemistry where appropriate.



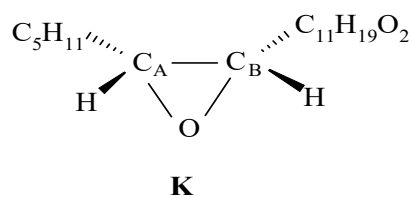
(4 marks)

1.9 Write the IUPAC name of Bombykol with stereodescriptors.

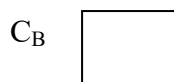
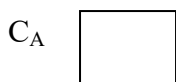


(1 mark)

Bombykol can be synthesized commercially from vernolic acid, (**K**) ( $C_{18}H_{32}O_3$ ), a constituent of the seed oil of *Euphorbia lagascae*.

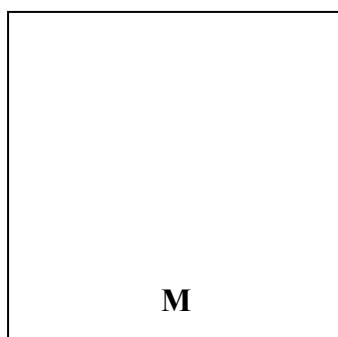
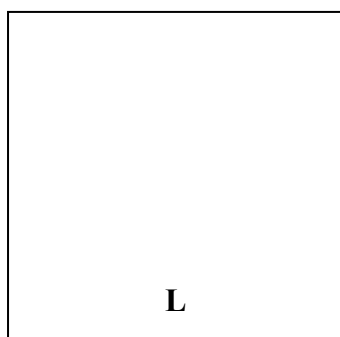


1.10 Assign stereodescriptors to  $C_A$  and  $C_B$ .



(2 marks)

1.11 Acid hydrolysis of vernolic acid is the first step in the synthesis of Bombykol. The reaction occurs through an *anti* (*trans*) addition to give two isomeric compounds **L** and **M**. Write the Fischer projection formulae of **L** and **M**.



(2 marks)

A neutral, optically inactive epoxy compound (**N**), isomeric with vernolic acid ( $C_{18}H_{32}O_3$ ), shows only 3 singlets in its  $^1H$ -NMR spectrum at  $\delta$  1.05, 1.50 and 2.54 with a relative intensity ratio of 9:6:1, respectively. (Relevant NMR data is given in table below).

1.12 Draw a possible structure of compound **N**.



(3 marks)

Table: Approximate  $^1H$  chemical shifts ( $\delta$ ) of some protons.

alkyl -H	0.9 - 1.5		4.0 - 4.5
	2.0 - 2.7		4.0 - 7.0
	2.5 - 2.7	R - O - H	4.0 - 8.0
	3.3 - 3.9		

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## Problem 2

17 marks

## Chemistry of Carbon Acids

A compound that contains a relatively acidic hydrogen bonded to a carbon is called a 'carbon acid'. The acidity of aldehydes, ketones, and esters is particularly important because their conjugate bases, known as *enolate ions*, are key reactive intermediates in many important reactions of carbonyl compounds.

2.1 Diethyl malonate (A) is a carbon acid.



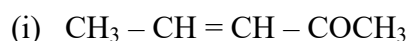
(A)

Structure of the conjugate base of diethyl malonate is

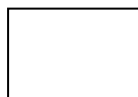


(0.5 mark)

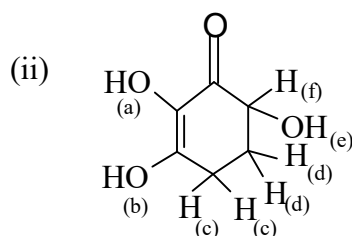
2.2 The most acidic hydrogens in the following compounds are



(a) (b) (c) (d)

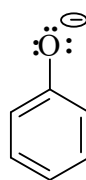
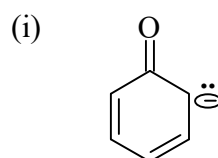


(0.5 mark)

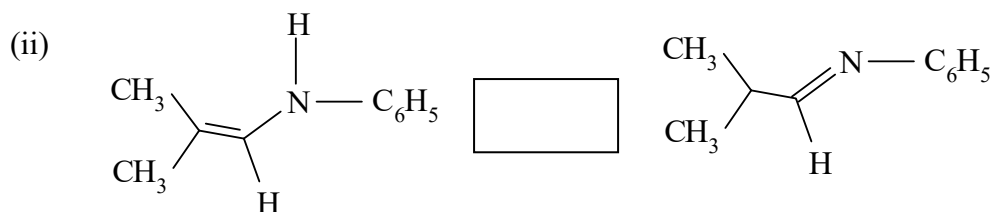


(0.5 mark)

2.3 Draw the correct symbols in the boxes to indicate the relationship between the following pairs of structures.



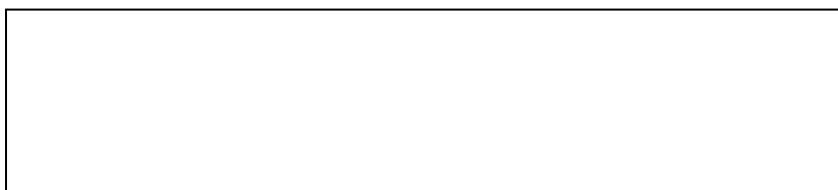
(0.5 mark)



(0.5 mark)

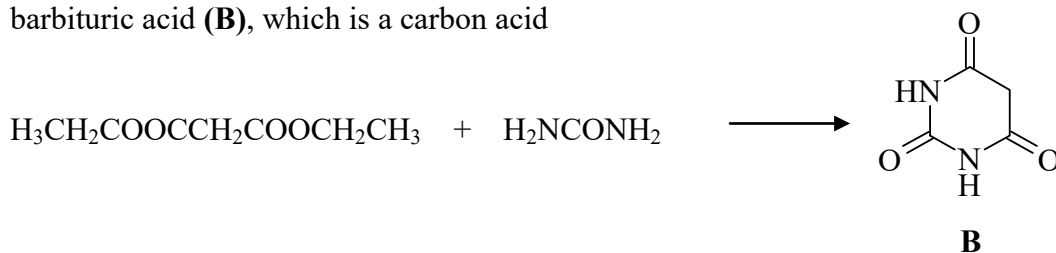
- 2.4  $^1\text{H}$  NMR spectrum of a commercial sample of dimedone (5,5-dimethylcyclohexan-1,3-dione) in  $\text{CDCl}_3$ , gives a signal at  $5.4 \delta$  and a broad peak at  $8.2 \delta$ , in addition to the peaks due to the methyl and the methylene groups. The structure of the compound responsible for the spectrum is

(Note: Relevant NMR data is given in the table on Page 36)

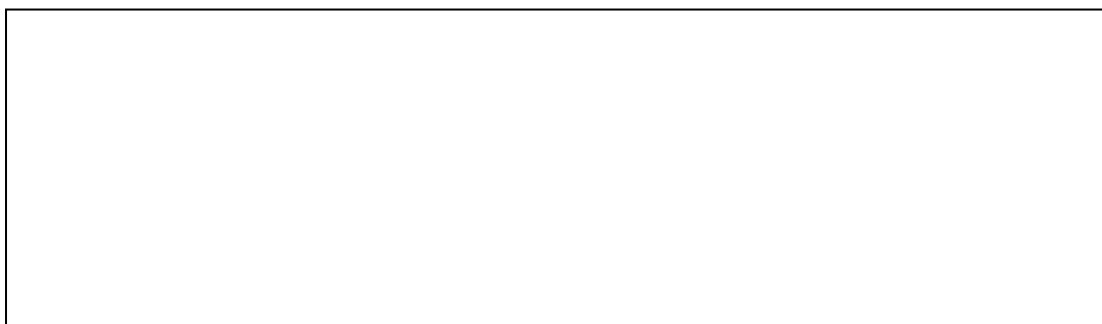


(1 mark)

- 2.5 Diethyl malonate on condensation with urea in the presence of sodium ethoxide yields barbituric acid (**B**), which is a carbon acid



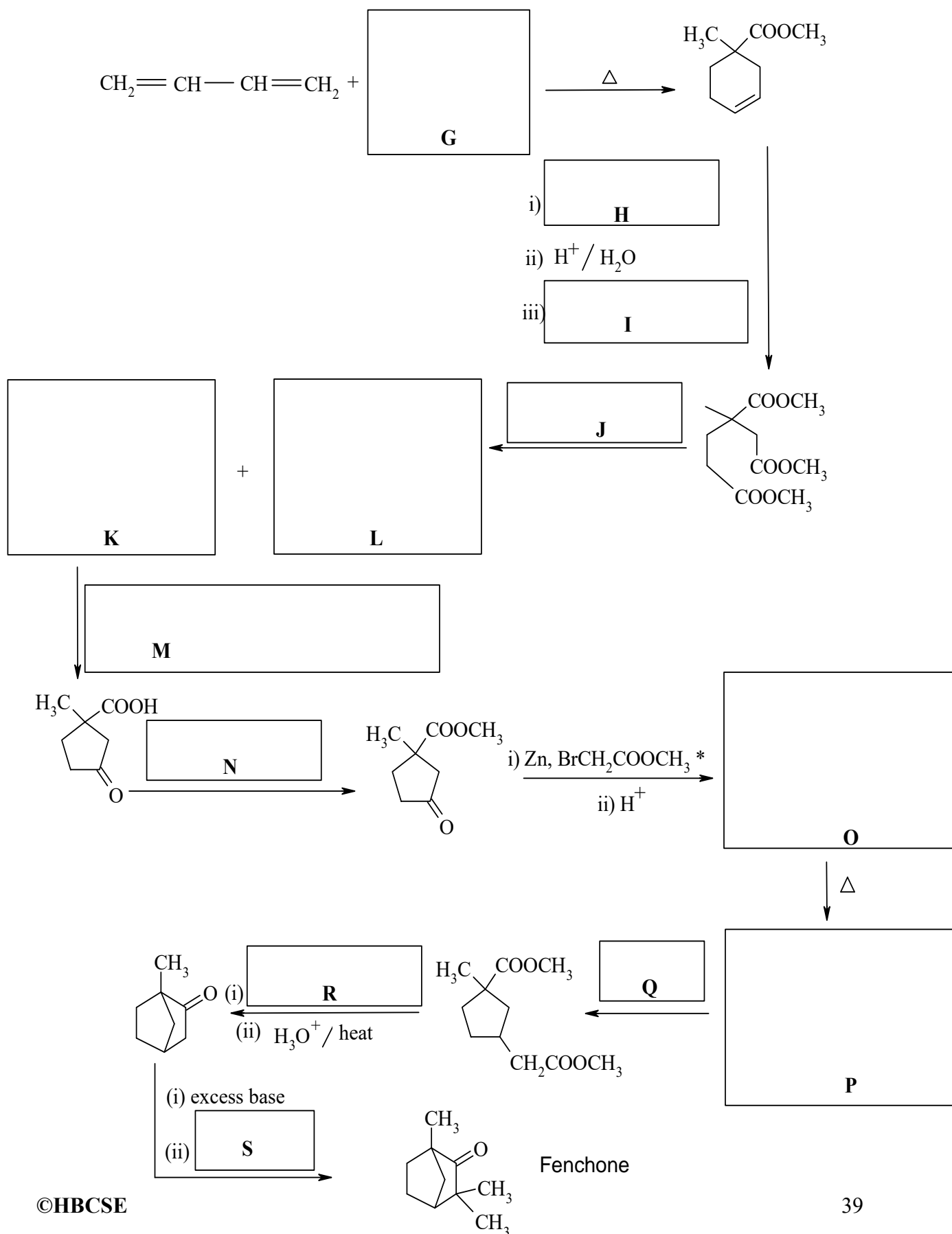
Draw the tautomeric forms of barbituric acid and identify the most stable form.



(2 marks)

- 2.6 Enolates are common intermediates in carbon-carbon bond formation reactions. Reactions that form carbon-carbon bonds are important to synthetic chemists as they provide pathways for the synthesis of large organic molecules from smaller ones.

(±) Fenchone, a terpenoid isolated from fennel oil, has been prepared by the following route. Draw the structures of the missing reagents and intermediates.





- \*  $\alpha$ -haloesters and Zn metal react to form an organozinc reagent analogous to the Grignard reagent

(7 marks)

- 2.7 The number of stereoisomers possible for Fenchone is

(0.5 mark)

- 2.8 The IUPAC name of Fenchone is

(1.5 marks)

- 2.9 The strongest peak in the IR spectrum of Fenchone would be due to

(1 mark)

- 2.10 Bases play an important role in enolate chemistry. The concentration of enolate depends on the pK<sub>a</sub> of the carbonyl compound and the basicity of the base used. Match the bases given in **column A** with suitable entries in **column B** (write the correct number against the alphabet given in the box).

**Column A**

- (a)  $\text{I}^-$   
(b)  $[(\text{CH}_3)_2\text{CH}]_2\text{N}^-$   
(c)  $\text{NH}_2^-$   
(d) 2,4,6 - trinitroaniline

**Column B**

- (i) strong base, weak nucleophile  
(ii) strong base, strong nucleophile  
(iii) weak base, weak nucleophile  
(iv) weak base, strong nucleophile

(a)	(b)	(c)	(d)
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(1.5 marks)

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**Problem 3****14 marks****Chemical Kinetics**

Nitrogen oxides ( $\text{NO}_x$ ) contribute to various environmental hazards. The primary sources of  $\text{NO}_x$  are motor vehicles, industrial and commercial units that burn fossil fuels.  $\text{NO}_x$  emission is mainly responsible for ozone smog, acid rain, and many other pollution related problems. Hence, researchers worldwide are actively engaged in  $\text{NO}_x$  pollution abatement. Various reductants like  $\text{H}_2$ ,  $\text{NH}_3$  and  $\text{CO}$  have been identified and approved by Environmental Protection Agency (EPA) to convert nitrogen oxides to  $\text{N}_2$ .

- 3.1 Write the stoichiometric equation for the reduction of  $\text{NO}$  to  $\text{N}_2$  by  $\text{H}_2$ .

**(0.5 mark)**

Kinetics of reduction of  $\text{NO}$  with  $\text{H}_2$  has been extensively studied, both in the gas phase and also on several acidic catalyst surfaces.

- 3.2 Write the expressions for the rate of formation of  $\text{N}_2$  and rate of consumption of  $\text{NO}$  in terms of their respective partial pressures  $P_{\text{N}_2}$  and  $P_{\text{NO}}$ .

**(0.5 mark)**

The reduction reaction of  $\text{NO}$  was carried out in the gas phase at  $820^\circ\text{C}$  at various initial partial pressures of  $\text{NO}$  and  $\text{H}_2$  and the initial rates of the reduction reaction were measured. The results of several such experiments carried out are given below in **Table I**.

Table I

Run	P <sub>NO</sub> (torr)	P <sub>H<sub>2</sub></sub> (torr)	Initial rate of formation of N <sub>2</sub> (torr sec <sup>-1</sup> )
1	20	40	0.0016
2	40	40	0.0064
3	25	25	0.00154
4	25	50	0.00306
5	50	50	0.01230

- 3.3 For most of chemical reactions, the rate ( $v$ ) can be given as  $v = k[A]^m [B]^n$ , where  $m$  and  $n$  are order of the reactants A and B. Using the data given in **Table I**, write the expression for the formation of N<sub>2</sub> in terms of P<sub>H<sub>2</sub></sub> and P<sub>NO</sub> and rate constant K.

(2 marks)

- 3.4 What is the unit of the rate constant?

(0.5 mark)

If in a reaction between two reactants A and B, the reactant B is present in large excess (at least 10 times more than A), the rate of the reaction can be expressed as  $\text{Rate} = k_{\text{app}} [A]^m$ , where  $k_{\text{app}} = k[B]^m$ , [A] and [B] are the respective concentration of reactants A and B.

- 3.5 Write the rate equation for the consumption of NO when  $P_{\text{NO}} = 600$  torr and  $P_{\text{H}_2} = 10$  torr.

(0.5 mark)

- 3.6 What is the unit of  $k_{\text{app}}$ ?

(0.5 mark)

The half life ( $t_{1/2}$ ) of any reactant is the time taken for that reactant to reach half of its initial concentration, when the reactant is not present in large excess initially. For a rate equation of the type,  $\text{rate} = k [A]^n$ ,  $t_{1/2} = \ln 2/k$  and  $1/A_0 k$  for  $n = 1$  and  $2$ , respectively, where  $A_0$  is the initial concentration of the reactant A whose rate of conversion is monitored. The  $t_{1/2}$  values of NO reduction at  $820^\circ\text{C}$  and at different initial partial pressures of the reactants have been calculated and given in **Table II**.

- 3.7 Insert the missing  $t_{1/2}$  values in **Table II**.

**Table II**

Run	$P^\circ_{\text{NO}}$ (torr)	$P^\circ_{\text{H}_2}$ (torr)	$t_{1/2}$ sec
1	600	10	19.1
2	600	20	?
3	10	600	830
4	20	600	?

(2 marks)

3.8 What is the rate constant of the reaction at 820°C?

(1 mark)

The differential rate equation for the consumption of  $H_2$  can be formulated from the deduced orders of NO and  $H_2$  and can be integrated to get the dependence of the partial pressures of NO and  $H_2$  on reaction time.

3.9 Deduce the expression for  $P_{H_2}$  as a function of time, if  $P_{NO}^0 = 2P_{H_2}^0$ , where  $P_{NO}^0$  and  $P_{H_2}^0$  are the initial pressures of NO and  $H_2$ , and  $P_{H_2}$  is the pressure of  $H_2$  at any time  $t$ .

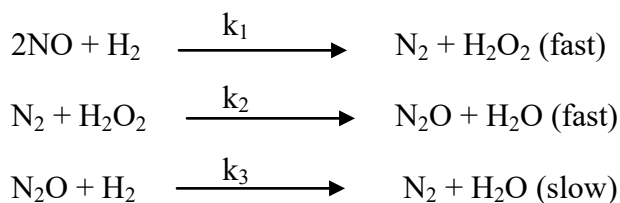
(1.5 marks)

- 3.10 What is the  $t_{1/2}$  of  $H_2$  under these partial pressures and if the reaction is carried out at  $820^\circ C$ ?

(1.5 marks)

Often, the mechanism of a chemical reaction can be deduced from the kinetic studies. The mechanistic scheme is written and one of the steps is assumed to be considerably slow, and the rate of the overall reaction can be expressed in terms of the rate of this step, known as the rate determining step. The rate equation obtained based on a proposed mechanism must be compatible to the experimentally derived rate equation. The theoretical rate equations can be computed using some approximations. One such is the steady state approximation, which assumes that the concentration of a reactive intermediate remains constant once it had reached a steady state. The method was originally developed by Bodenstein in 1913 according to which if a reaction involves a reactive intermediate B, at steady state,  $d[B]/dt = 0$  i.e., rate of formation of B equals its rate of decomposition at steady state.

The following mechanism can be proposed for the  $NO + H_2$  reaction as



- 3.11 Assuming that  $N_2O$  and  $H_2O_2$  are in steady state, write the expressions for the net rate of formation of  $N_2O$  and  $H_2O_2$ .

(1 mark)

3.12 What is the expression for the rate of the slow step of the reaction?

(1 mark)

3.13 Write the expression for the rate of the reaction using the expressions for the steady state concentrations.

(1 mark)

3.14 Based on the kinetic observation, is this an acceptable mechanism? (Mark the correct box)

Yes  No

(0.5 mark)

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**Problem 4****13 marks****Solubility Equilibria**

To keep the water pure (free from bacteria and algae) for swimmers, generally chlorine is added to swimming pool water. The permissible value of chloride ions in such water is 2 ppm (2mg/L). One of the methods to estimate chloride concentration in such samples involves titration with  $\text{AgNO}_3$  using  $\text{K}_2\text{CrO}_4$  as indicator.

In a typical analysis, a 100 mL sample was drawn from the swimming pool. 25 mL of the water sample was titrated with 0.0017 M  $\text{AgNO}_3$  using  $\text{K}_2\text{CrO}_4$  indicator. The titrant reading was 14.5 mL when a brick red precipitate was formed.

( $K_{\text{sp}}$  of  $\text{AgCl} = 1.78 \times 10^{-10}$ ,  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4 = 1.10 \times 10^{-12}$ )

- 4.1 Write balanced equations for the reactions involved in the titration and responsible for the observed brick red precipitation.

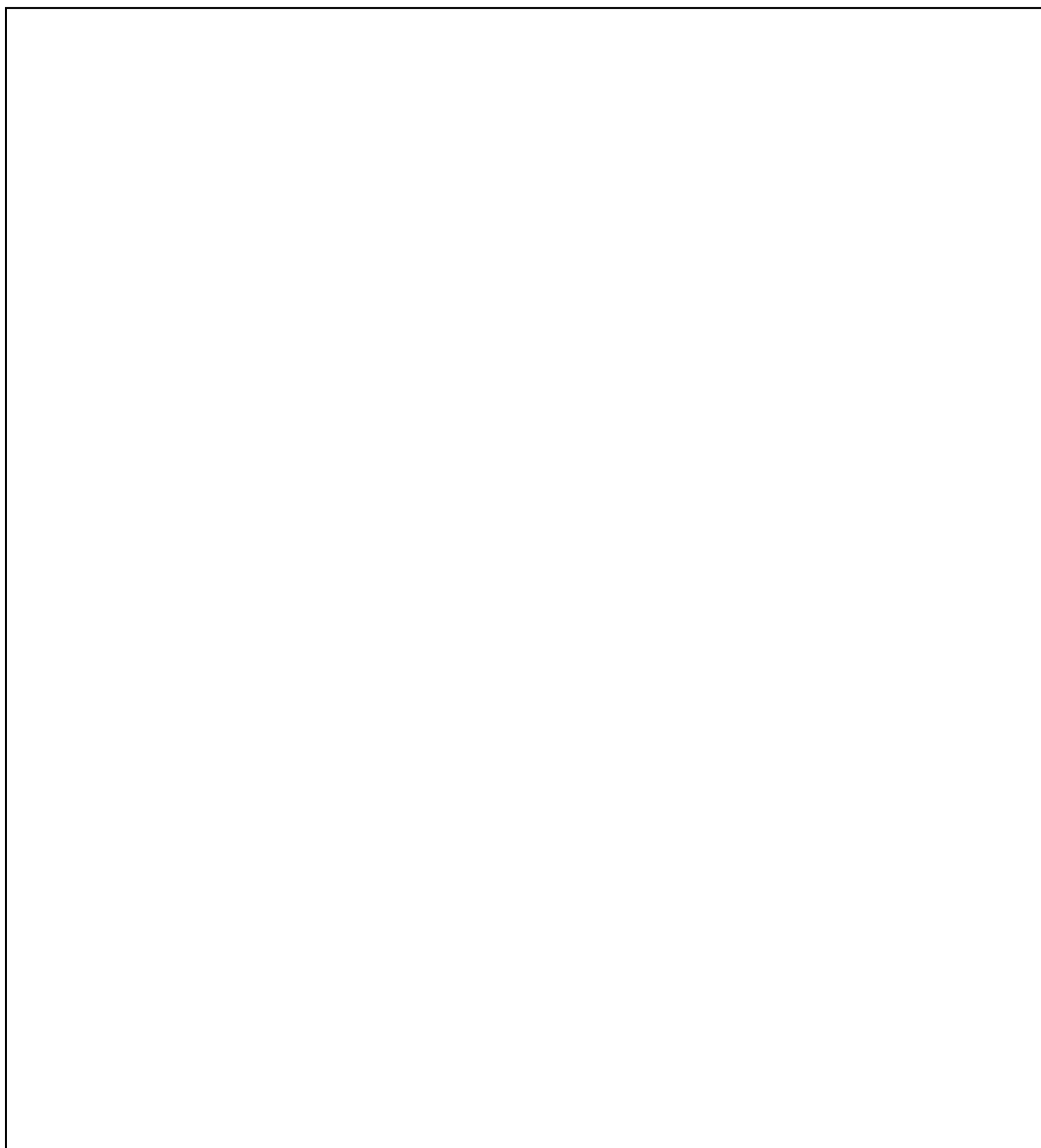
**(1 mark)**

- 4.2 What is the amount of chloride in grams in the 100 mL of the collected sample?

**(1.5 marks)**



- 4.3 In another titration, 25 mL of 0.050 M  $\text{Cl}^-$  was titrated with 0.050 M  $\text{Ag}^+$ . Calculate the  $\text{Ag}^+$  concentration in the mixture when i) 24.98 mL and ii) 25.02 mL of the  $\text{AgNO}_3$  is added. Calculate the range of chromate ion concentrations needed for the formation of brick red precipitate for these two cases.



(3 marks)

- 4.4 Generally the indicator concentration used in the actual titrations is 0.005 M. Calculate the concentration of chloride in the solution when the red precipitate is formed.

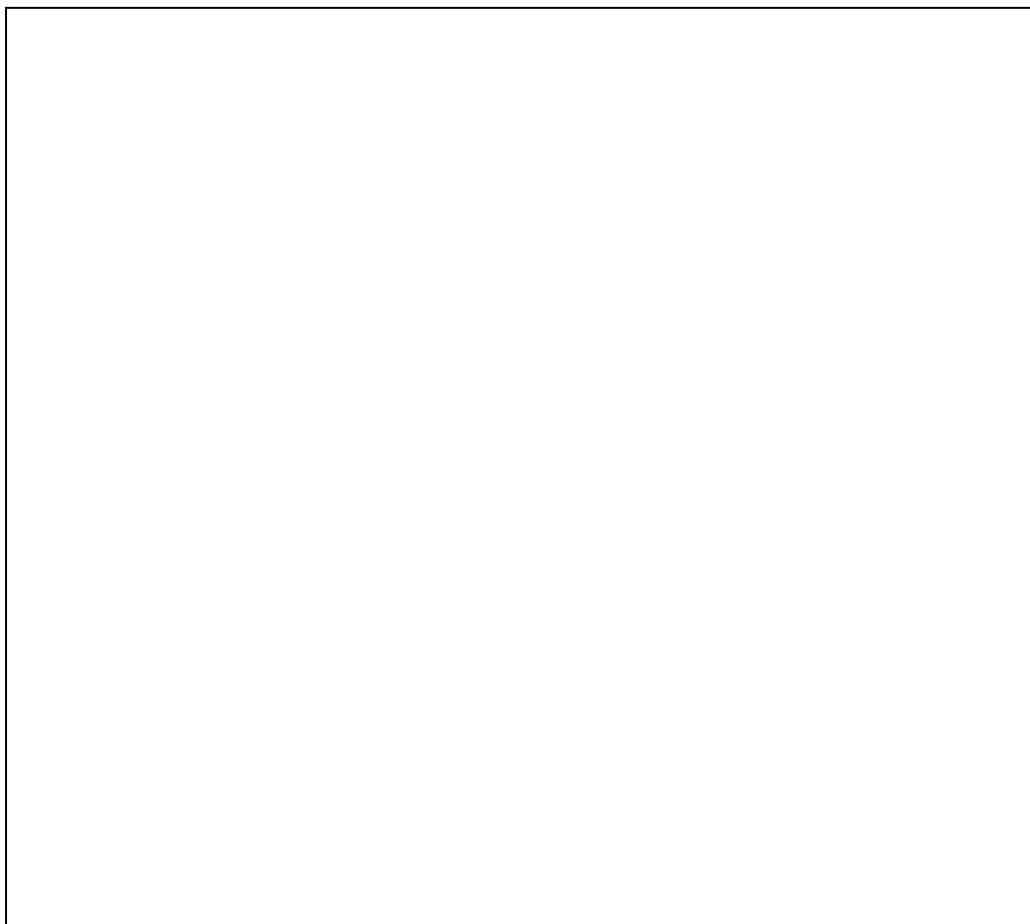
(3 marks)

- 4.5 For this titration to work most efficiently, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium influencing the observed endpoint of this titration.

(1.5 marks)

- 4.6 Typically for the above titration, a buffer is added to establish and maintain a pH of 7.15 in aqueous medium. Choose an appropriate buffer system from the list below. Show the calculations which lead to your choice.

Buffer systems	$K_a$ of weak acid
(a) 0.50 M lactic acid / 0.20 M sodium lactate	$1.4 \times 10^{-4}$
(b) 0.70 M acetic acid / 0.30 M sodium acetate	$1.8 \times 10^{-5}$
(c) 0.50 M sodium dihydrogen phosphate / 0.15 M sodium hydrogen phosphate	$6.2 \times 10^{-8}$
(d) 0.8 M ammonium chloride / 0.3 M ammonia	$5.6 \times 10^{-10}$



**(2 marks)**

- 4.7 Using the selected buffer system, calculate the number of grams of weak acid and of conjugate base you would need to dissolve in distilled water to prepare 500 mL of buffer with pH 7.15.

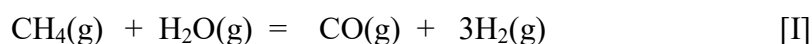


**(1 mark)**

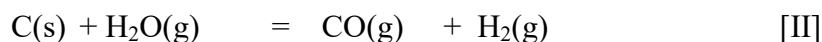
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**Problem 5****18 marks****Molecular Hydrogen**

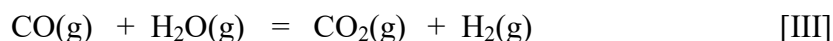
Molecular hydrogen is not present in significant quantity in the earth's atmosphere. The main commercial process for the production of hydrogen is steam reforming (I), viz. the catalyzed reaction of water and hydrocarbons, typically methane, at high temperatures.



A similar reaction, but with coke as the reducing agent, is called as the water gas reaction (II).



Both reactions are generally followed by a second reaction known as the Shift reaction (III), in which, water is reduced to hydrogen by carbon monoxide.



Hydrogen production is often integrated with processes that need hydrogen as the feedstock.

- 5.1** Using the values given in **Table I, Pg-55**, calculate the equilibrium constants for the reactions II and III. (Show the calculations involved).

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(5 marks)

5.2 On the basis of the values obtained for the equilibrium constants of the two reactions which of the statements would be correct?

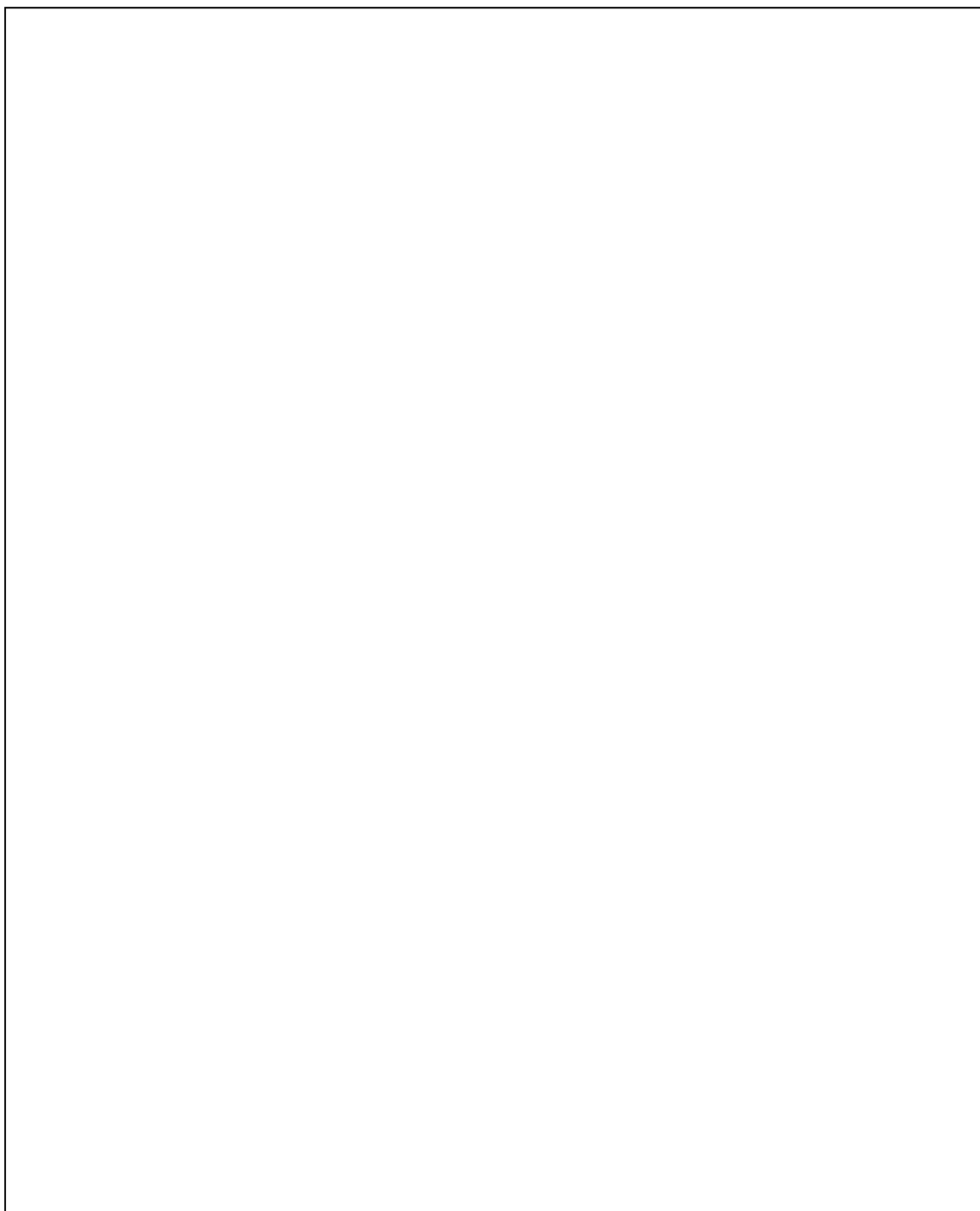
- (i) Reaction II is spontaneous whereas III is not.
- (ii) Both reactions II and III are spontaneous.
- (iii) When the reactants are mixed in the case of reaction II the reaction will go to completion whereas in the case of reaction III the equilibrium will lie towards left.
- (iv) Reaction III is spontaneous whereas II is not.

(1 mark)

5.3 What will be the change in the equilibrium composition of the system in case of reaction III, if the pressure on the system is doubled keeping temperature constant?

(1 mark)

- 5.4 With the help of the supplied  $C_p$  values (Table II, Pg-55) obtain a relation between the equilibrium constant for the reaction III at temperature T and that at 298 K.



(5 marks)

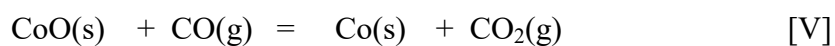
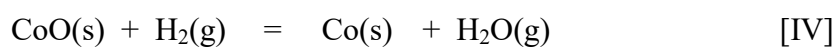
5.5 Hence, calculate the equilibrium constant for the reaction III at 1200K.

(2 marks)

5.6 Calculate the equilibrium composition if the feed mixture for reaction III contains 50 mole percent of CO and 50 mole percent of water.

(2 marks)

5.7 To the reaction system that has reached equilibrium in (5.6), CoO(s) and Co(s) are added. This leads to two more equilibria in the system.



The equilibrium mixture, on analysis, was found to contain 30 mole percent of water. Calculate the equilibrium constants for the reactions IV and V.

(2 marks)

**Table I**

	$\Delta H^\circ_f$ kJ mol <sup>-1</sup>	$S^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>
CO	-110.4	197.7
CO <sub>2</sub>	-393.1	213.4
H <sub>2</sub>	----	130.5
H <sub>2</sub> O	-241.6	188.6
C (g)	---	5.68

**Table II**

	$C_p$ in Jmol <sup>-1</sup> K <sup>-1</sup>
CO	$27.6 + 5.0 \times 10^{-3} T$
CO <sub>2</sub>	$21.6 + 6.3 \times 10^{-2} T$
H <sub>2</sub>	$27.7 + 3.4 \times 10^{-3} T$
H <sub>2</sub> O	$30.2 + 9.9 \times 10^{-3} T$



Name of Student

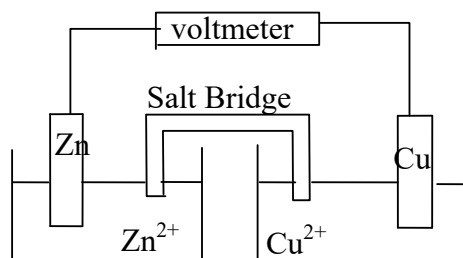
Centre

## Problem 6

10 marks

## Electrochemistry

The most popular electrochemical cell, Daniel cell was originally developed by the English chemist John F. Daniel. The general assembly of the cell is as given below



An undergraduate student sets up a Daniel cell using  $100\text{cm}^3$  of  $0.100\text{M}$   $\text{CuSO}_4$  and  $0.100\text{M}$   $\text{ZnSO}_4$  solutions respectively. The two compartments are connected by a suitable salt bridge.

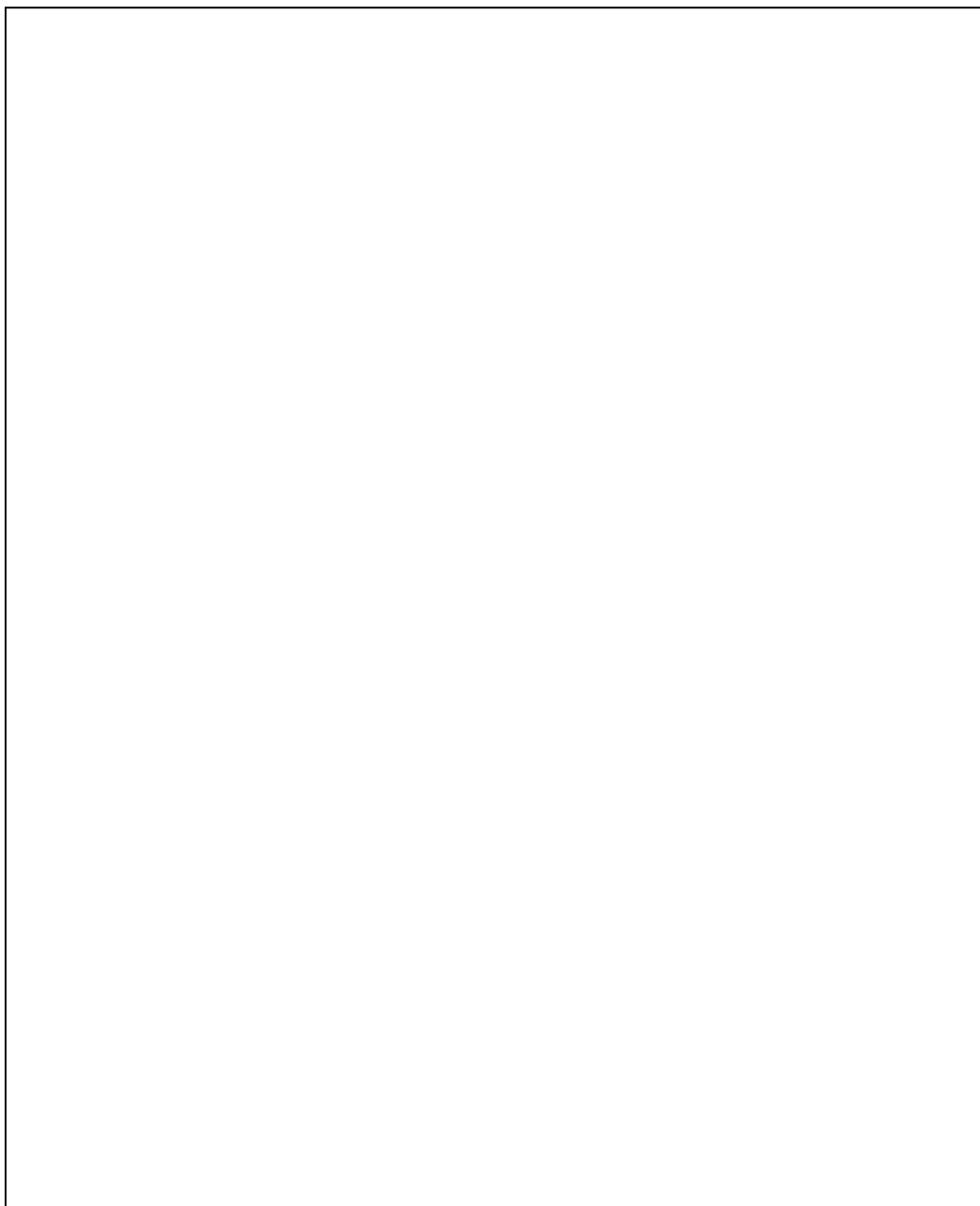
- 6.1 Calculate the emf of the above cell (Refer to **Table I**). Assume the temperature of the laboratory to be  $25^\circ\text{C}$  and the solutions are dilute enough so that molar concentrations can be used instead of activities of the solutions)

(0.5 mark)

A lab mate of the student asked her for some solid  $\text{CuCl}_2$ . While she was lifting the bottle from a shelf, the lid of the bottle slipped and some amount of  $\text{CuCl}_2$  fell in the  $\text{CuSO}_4$  compartment. She measured the emf of the cell again and found that it had

increased by 9mv. She used this data to calculate the amount of  $\text{CuCl}_2$  that had spilt in the compartment.

- 6.2 Calculate the mass of  $\text{CuCl}_2$  in grams that had spilt into the Daniel cell? (Molecular mass of  $\text{CuCl}_2 = 134.45 \text{ g}$ ).



(2.5 marks)

After making this calculation, the student discarded the solutions from both the compartments and washed the cell thoroughly. She refilled the compartments with  $100 \text{ cm}^3$  of the original  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  solutions. A current of 10 mA was drawn from the cell for a period of 2.77 hours.

6.3 What will be the molar concentrations of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  after 2.77 hours?

(2 marks)

A galvanic cell in which the potential is developed due to the difference in concentrations of the same electrolyte filled both cell compartments is known as a concentration cell. Such a cell uses identical electrodes in both the compartments.

The student decided to convert her early set up of the Daniel cell into a concentration cell. She now filled the two cell compartments with 2.50 M and 0.017 M of  $\text{CuSO}_4$  solutions respectively. She dipped clean Cu electrodes into these solutions and made the necessary connections to complete the cell.

6.4 What is the value of  $E^\circ$  of this cell?

(0.5 mark)

- 6.5 Calculate the value of the cell potential.

**(1mark)**

Corrosion is the deterioration of a material due to interaction with its environment and is area of primary concern in engineering industry. Corrosion occurs due to the formation of a concentration cell when two or more portions of a metal are in contact with different concentrations of a solution. Rusting is an example of corrosion of iron in which metallic iron is oxidized to  $\text{Fe}^{2+}$  in presence of atmospheric oxygen and water. The atmospheric  $\text{O}_2$  is converted to  $\text{OH}^-$ .

- 6.6 Write the half cell reactions for corrosion of iron and write the overall chemical reaction.

**(2 marks)**

Rust is the reddish brown flaky  $\text{Fe}(\text{OH})_3$  formed on the surfaces.

- 6.7 Write the balanced chemical equation that leads to the formation of  $\text{Fe}(\text{OH})_3$ .

**(0.5 mark)**

Corrosion of iron can be prevented by coating the surface with another metal. The process of galvanization involves coating of iron with zinc whereas that of tinning involves coating of iron with tin.

- 6.8 State with reasons, which of these two processes should be preferred for preventing corrosion.

(1 mark)

**Table I:** Standard Electrode Potentials at 25°C.

System	$E^\circ / V$
$Cu^{2+}/Cu$	0.342
$Zn^{2+}/Zn$	-0.762
$Fe^{2+}/Fe$	-0.441
$Sn^{2+}/Sn$	-0.140

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## Problem 7

10 marks

## Chemistry of Boron

Boron trifluoride [BF<sub>3</sub>] has 6 valence electrons around the boron atom and hence it behaves as a Lewis acid. As we substitute fluorine by other halogens, the electron density on the boron atom changes significantly.

- 7.1 Predict the order of electron density on boron atom in various boron halides viz BF<sub>3</sub>, BCl<sub>3</sub>, BBr<sub>3</sub>, BI<sub>3</sub>.

(1 mark)

- 7.2 What should be the order of acidic character of these halides?

(0.5 mark)

- 7.3 The above order of acidity may be explained by considering it to be due to

(a) mismatch between size of boron atom and higher halogen atoms leads to poor overlap of p orbital, which leads to reduction in electron density on boron.

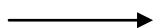
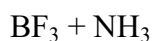
(b) decrease in electronegativity of halogens from F to I

(c) electron deficient nature of boron affected by B-X sigma bond

(d) more diffuse nature of p orbital in case of higher halogens.

(1 mark)

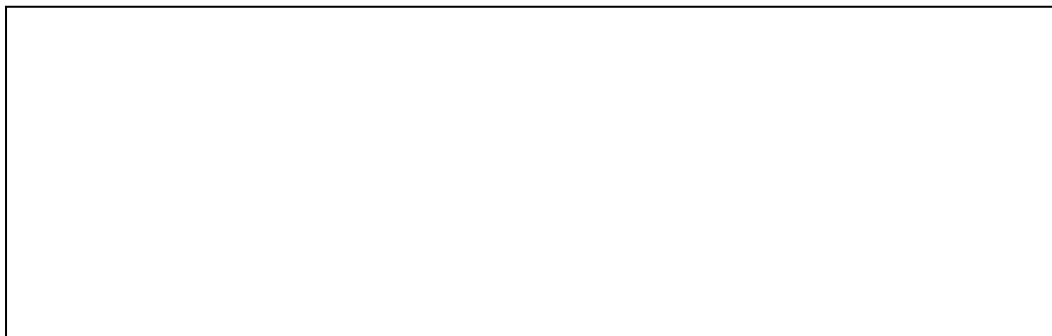
- 7.4 On the basis of above properties of boron halide, predict the product of the following reaction. Draw the Lewis structure of the product.



Lewis structure

(0.5 mark)

- 7.5  $\text{BH}_3$  exists as a dimer (diborane) because of the electron deficient character of the boron atom. Write the structure of the product for the reaction of diborane with excess ammonia under ambient conditions.



(1 mark)

- 7.6 Diborane molecule has the following type of bonds. Mark the correct answer.

- (a) 2 two center- 2 electron bonds and 2 three center- 2 electron bonds
- (b) 4 two center- 2 electron bonds and 2 three center- 2 electron bonds
- (c) 2 two center- 2 electron bonds and 4 three center- 2 electron bonds
- (d) 3 two center- 2 electron bonds and 3 three center- 2 electron bonds

(1 mark)

- 7.7 Borazine [ $\text{B}_3\text{N}_3\text{H}_6$ ], which is also called inorganic benzene, is isoelectronic with benzene. It is prepared by reaction of boron trichloride and ammonium chloride at a high temperature. Draw its structure, clearly indicating the nature of bonds and their polarization.



(1 mark)

- 7.8 Benzene and borazine have many similarities in properties, but they do have certain differences. For example, benzene does not react with HBr but borazine does. Write the molecular formula and draw the structure of the product formed in the reaction of borazine with HBr.



(2 marks)

- 7.9 Boron hydrides include simple polyhedral *closo* compounds and progressively more open *nido* and *arachno* structures. British Chemist Kenneth Wade established a correlation between skeleton electrons and the geometry for boranes, viz.

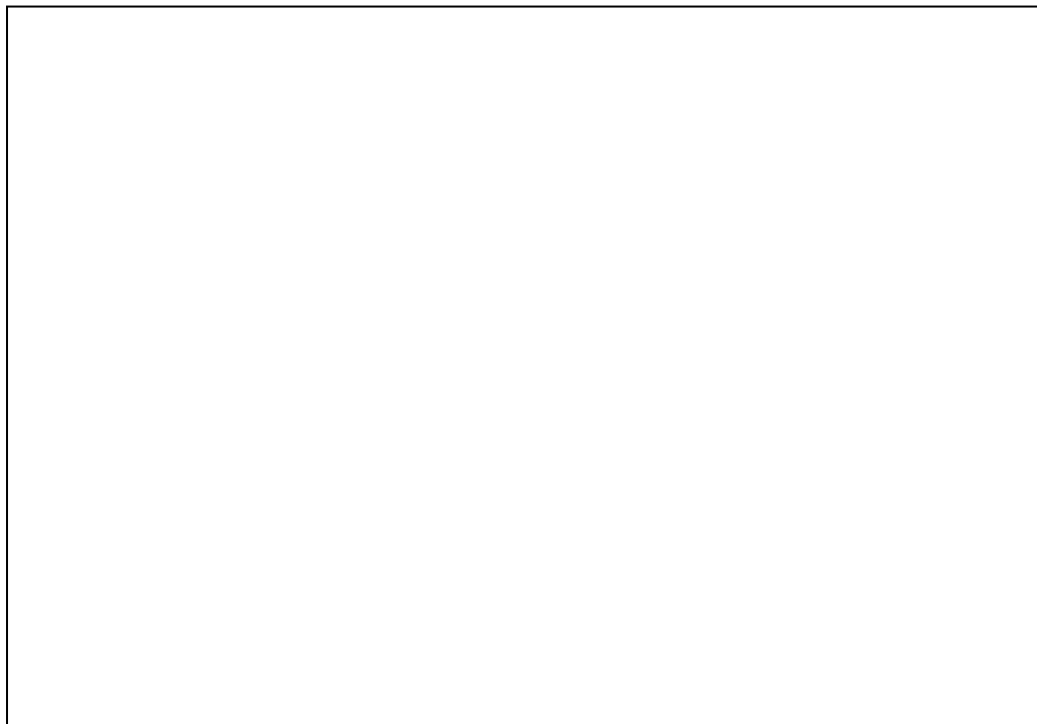
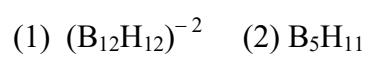
Type	Skeletal electron pairs
<i>Closo</i>	$n + 1$
<i>Nido</i>	$n + 2$
<i>Arachno</i>	$n + 3$

wherein  $n$  = number of B-H units

For example, in the case of  $B_2H_6$ , each of the two B-H units contributes 2 electrons and additional, 4 hydrogens contribute 4 electrons. Therefore, this molecule has total 8 electrons, and since  $8 = 2(n + 2)$ ,  $B_2H_6$  molecule has *nido* structure.



Based on this correlation, predict the structures of the following boranes:



(2 marks)

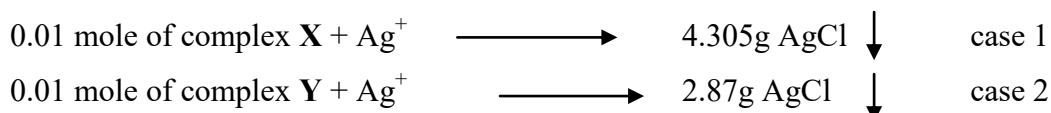
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**Problem 8****23 marks****Chemistry of chromium and nickel**

Chromium and nickel are important elements in the first transition metal series. They have very large number of applications such as electroplating, manufacturing of stainless steel or nichrome wires for electrical heating.

**Part A**

Chromium forms variety of isomeric complexes. Two complexes X & Y have same empirical formula  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . When these complexes are treated with excess of  $\text{AgNO}_3$ , different quantities of  $\text{AgCl}$  are obtained.



Based on this information

- 8.1 Calculate the number of moles of  $\text{AgCl}$  in the cases (1) and (2)

**(1 mark)**

- 8.2 Write the formulae, IUPAC names and draw the structures of complexes X & Y

**(3 marks)**

8.3 Complexes **X** and **Y** are isomers of one of the following types. Mark the correct answer.

- (a) hydrate
- (b) linkage
- (c) ionization

(0.5 mark)

8.4 The conductivities of 0.001M solution of complexes **X** and **Y** are measured. Mark the correct choice assuming 100% ionization.

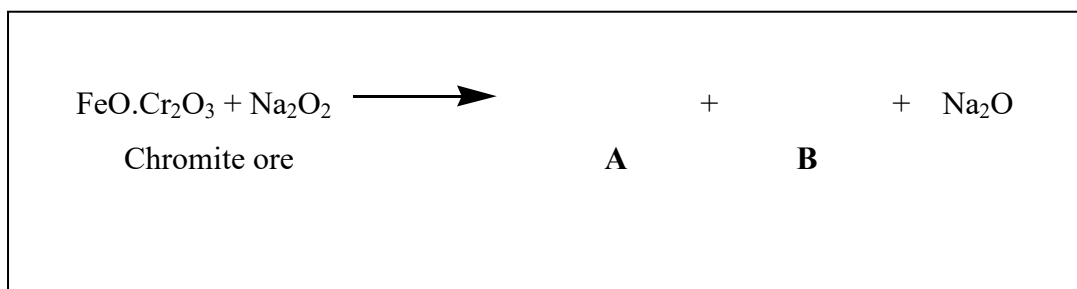
- (a) conductivity of complex **X** is greater than that of complex **Y**.
- (b) conductivity of complex **X** is less than that of complex **Y**.
- (c) conductivity of complex **X** is equal to that of complex **Y**.

(0.5 mark)

**Part B**

Chromite ore  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  is fused with excess of sodium peroxide ( $\text{Na}_2\text{O}_2$ ). In this process, both iron and chromium are converted to their oxo anions **A** and **B** respectively and  $\text{Na}_2\text{O}$  is formed.

8.5 Write the balanced equation for the above reaction.



(2 marks)

8.6 The melt of above fusion is then leached with water. It is found that **A** reacts with water to give a red brown precipitate **C** while **B** dissolves in water to give a yellow coloured solution containing species **D**. The solution on acidification turns orange due to formation of **E**. Write balanced equations for all the reactions leading to above observations.

(2 marks)

8.7 Draw structures of **D** and **E**.

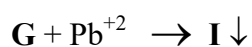
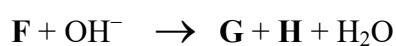
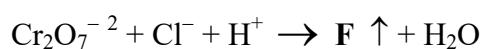
(2 marks)

8.8 Orange colour of **E** is due to

- (a) d-d transition
- (b) charge transfer transition
- (c) n to  $\pi^*$  transition

(0.5 mark)

8.9  $K_2Cr_2O_7$  is used to confirm the presence of  $Cl^-$  ion in a sample. The reactions involved are given below.



Yellow precipitate

Identify **F**, **G**, **H**, **I** and write the balanced equations.

(1.5 marks)

- 8.10** Chromate ions present in effluents from chrome plating plants, tanneries etc. are estimated using dithionate ion  $(S_2O_4)^{-2}$ . Dithionate ion  $(S_2O_4)^{-2}$  reduces chromate ion in an alkaline medium to insoluble chromium hydroxide and itself gets oxidized to sulphite ion. Write the balanced equation for this reaction.

(1 mark)

- 8.11** 1 L of effluent containing  $CrO_4^{-2}$  requires 3.87 g of  $Na_2S_2O_4$  for completion of the above reaction. Calculate the molarity and normality of  $CrO_4^{-2}$  ions. Also express the concentration of the  $CrO_4^{2-}$  ions in ppm.

(2.5 marks)

**Part C**

- 8.12**  $[Ni(Cl)_4]^{-2}$  is paramagnetic in nature while  $[Ni(CN)_4]^{-2}$  is diamagnetic. Based on valence bond theory, predict the hybridization and geometries of these Nickel complexes. Draw the orbital diagrams indicating the distribution of electrons for i) free metal ion and ii) metal ion in the complexes.

(3 marks)

- 8.13** Aqueous solution of complex  $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$  (**J**) is of green colour. On addition of excess ethylenediamine (en)  $[\text{en} = \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2]$ , color of the solution changes to violet due to formation of complex **K**. Write balanced equation of the reaction responsible for the observed colour change.

(0.5 mark)

- 8.14** The complex **K** exhibits isomerism of the type.

- (a) geometrical
- (b) geometrical and optical
- (c) optical

(0.5 mark)

8.15 Draw the structures of all possible isomers of **K**.

(1 mark)

8.16 From the **Table I** estimate the  $\lambda_{\max}$  for the complexes **J** and **K**.

(1 mark)

8.17 Which of the following statements about the crystal field splitting  $10Dq$  is correct?

- (a)  $10Dq$  of en  $>$   $10Dq$  of  $H_2O$
- (b)  $10Dq$  of en  $<$   $10Dq$  of  $H_2O$
- (c)  $10Dq$  of en =  $10Dq$  of  $H_2O$

(0.5 mark)

**Table I**

Wavelength nm	Colour absorbed	Complementary colour
400	Violet	Yellow green
450	Blue	Yellow
490	Blue green	Orange
500	Green	Red
570	Yellow green	Violet
580	Yellow	Blue
600	Orange	Blue green
650	Red	Green