Instructions for students

- Write your name and roll no. at the top of the first pages of all problems.
- This examination paper consists of 39 pages of problems including answer boxes.
- You have 3 hours to complete all the problems.
- Request the supervisor to provide you with rough sheets for rough work.
- **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.
- For calculations, you must show the main steps.
- Use only a non-programmable scientific calculator.
- For objective type questions: Mark **X** in the correct box. Some of the objective questions may have more than one correct choice.
- Values of fundamental constants required for calculations are provided on page 2.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.
- Do not leave the examination room until you are directed to do so.
- The question paper will be uploaded on the HBCSE website by 31^{st} January 2010.

Fundamental Constants

Avogadro constant	$N_A = 6.022 \times 10^{23}\ mol^{-1}$
Electronic charge	$e = 1.602 \times 10^{-19}$ C
Molar gas constant	$R = 8.314\ J\ K^{-1} mol^{-1}$
	$= 8.314\ K\ Pa.dm^3\ K^{-1} mol^{-1}$
	$= 0.082\ L.atm\ K^{-1} mol^{-1}$
1 atomic mass unit (1u)	$= 931.5\ MeV/c^2$
1 eV	$= 1.602 \times 10^{-19}$ J
Rydberg constant	$R_H = 2.179 \times 10^{-18}$ J
Mass of electron	$m_e = 9.109 \times 10^{-31}$ kg
Planck's 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	$= 13.6 \times 10^3\ kg\ m^{-3}$

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Problem 1 **17 marks**

Thermal and photolytic decomposition of Acetaldehyde

The stoichiometric equation for the pyrolysis of acetaldehyde to methane and carbon monoxide is as follows: $CH_3CHO \rightarrow CH_4 + CO$

1.1 (a) The order of this reaction determined experimentally was 1.5. Write the rate equation for the reaction.

(0.5 mark)

(b) If v is the rate corresponding to $P_{CH_3CHO} = P_1$, what is the (i) order and (ii) rate of reaction, when $P_{CH_3CHO} = 4P_1$?

(1 mark)

1.2 The pyrolysis of acetaldehyde under certain conditions, can be an intramolecular process. What products are formed in the pyrolysis of a mixture of CH_3CHO and CD_3CDO?

(1 mark)

1.3 The major steps in the gas phase thermal pyrolysis of acetaldehyde, as identified by Rice and Herzfeld are as follows

$CH_3CHO(g) \xrightarrow{k_1} \bullet CH_3(g) + \bullet CHO(g)$ ....(i)

$\bullet CH_3(g) + CH_3CHO(g) \xrightarrow{k_2} CH_4(g) + \bullet CH_3CO(g)$ ....(ii)

$\bullet CH_3CO(g) \xrightarrow{k_3} \bullet CH_3(g) + CO(g)$ ....(iii)

$2\ \bullet CH_3(g) \xrightarrow{k_4} C_2H_6$ ....(iv)

(a) Identify the propagation and termination steps from the above reactions.

(1 mark)

(b) Assuming $\bullet CH_3$ and $\bullet CH_3CO$ to be under steady state (i.e. the rate of formation and rate of consumption of an intermediate species are equal), derive expressions for (i) $[\bullet CH_3]$ and (ii) $[\bullet CH_3CO]$ in terms of $[CH_3CHO]$.

(2 marks)

(c) Deduce d [CO]/dt in terms of [CH_3CHO].

(1 mark)

1.4 (a) In the photochemical decomposition of acetaldehyde, one photon of absorbed light decomposes one molecule of CH_3CHO into $\bullet CH_3$ and $\bullet$CHO. If 'I_{abs}' is the intensity of light absorbed in the reaction,

(i) Write the rate equation for this photochemical decomposition. (Note: the first step in the photochemical reaction is temperature independent)

(ii) Calculate [$\bullet CH_3$] and d[CO]/dt assuming steps (ii) to (iv) given in **1.3** are same and [$\bullet CH_3$], [$\bullet CH_3CO$] are under steady state.

(1.5 marks)

(b) If C-C, C-H, and C=O bond energies in acetaldehyde are 377, 421 and 720 kJ mol^{-1} respectively, calculate the wavelength of radiation (in nm) required to bring about the photochemical decomposition of acetaldehyde.

(1 mark)

1.5 The Arrhenius (pre exponential) factors and activation energy values for steps (i) to (iv) in **1.3** are A_1, A_2, A_3, A_4 and E_1, E_2, E_3 and E_4 respectively.

(a) Calculate the overall activation energy $E_{thermal}$ for the thermal decomposition of acetaldehyde.

(1.5 marks)

(b) Write the expression for overall activation energy, $E_{photochemical}$ of photochemical decomposition of acetaldehyde.

(1 mark)

1.6 The recombination of methyl radicals has no activation barrier. The activation energy values for the first step in the thermal decomposition of acetaldehyde in **(1.3)** and $E_{photochemical}$ are 309.32 kJ mol^{-1} and 41.8 kJ mol^{-1} respectively.

(a) Calculate the overall activation energy for the thermal decomposition of acetaldehyde

(1 mark)

(b) Calculate the rate constant and rate of overall reaction for the thermal decomposition of acetaldehyde at 101 kPa and 800 K, if overall Arrhenius factor is 2.3×10^{12} $dm^{3/2}$ $mol^{-1/2}$ sec^{-1}.

(2 marks)

1.7 CH_3CHO can be formed from CH_3CH_2OH and further get oxidised to CH_3COOH as

$$CH_3CH_2OH \xrightarrow{k_5} CH_3CHO \xrightarrow{k_6} CH_3COOH$$

(a) Qualitatively sketch the concentration vs time plots of CH_3CHO, CH_3CH_2OH and CH_3COOH, till the reaction goes to completion.

(1.5 marks)

(b) If both the reactions in **1.7** are of 1st order, $[CH_3CHO]$ is related to initial concentration of alcohol $[CH_3CH_2OH]_0$ by the equation,

$$\frac{[CH_3CHO]}{[CH_3CH_2OH]_0} = \frac{k_5}{k_6 - k_5}(e^{-k_5 t} - e^{-k_6 t})$$

Derive the expression for $[CH_3CHO]$ in terms of $[CH_3CH_2OH]$ if $k_5 << k_6$.

(1 mark)

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Problem 2 **19 marks**

Chemistry of coordination compounds

Developments in the field of coordination chemistry have led to new concepts in chemical bonding and molecular structure, revolutionized the chemical industry and provided insight into functions and structures of vital components of biological systems. Coordination compounds find extensive applications in metallurgical processes, analytical and medicinal chemistry.

2.1 Anhydrous copper sulphate, a white solid, when dissolved in water, gives a blue coloured solution. On addition of dilute ammonia, a blue precipitate is obtained, which dissolves in excess of concentrated ammonia giving a deep blue solution. Write the chemical reactions involved in the formation of these coloured species.

(1.5 marks)

2.2 Most copper(I) compounds are found to be colourless. This is due to

a] presence of low oxidation state of copper. ☐

b] completely filled d-level in Cu(I). ☐

c] diamagnetic nature of the compound. ☐

d] high polarizability of Cu(I) ion. ☐

(0.5 mark)

2.3 The expected spin-only magnetic moments of complexes of a transition metal like nickel or cobalt depend on

a] oxidation state of the metal. ☐

b] nature of the ligand. ☐

c] geometry of the complex. ☐

d] number of unpaired electrons in free transition metal ion. ☐

(1 mark)

2.4 Ni^{2+} forms a variety of complexes with different ligands. Thus, it gives $[Ni(H_2O)_6]^{2+}$ with H_2O and $[NiCl_4]^{2-}$ with Cl^-. Both the complexes show paramagnetism corresponding to two unpaired electrons. Draw the crystal field splitting diagrams for the two complexes showing the d-electron distribution to explain the observed magnetic properties. State the geometries of the two complexes.

(2 marks)

2.5 a) Give IUPAC name of the complex $[CoCl_2(en)_2]^+$. (en = $H_2N-CH_2-CH_2-NH_2$) (complex **A**)

b) Draw the structures of the geometrical isomers of complex **A**.

c) Which of the geometrical isomers of complex **A** is/are optically active?

d) Give the structures of the optical isomers.

(2.5 marks)

2.6 Both Ni^{2+} and Pt^{2+} are d^8 ions. With Cl^- ligands, both form $[MCl_4]^{2-}$ complex ions. However, while $[NiCl_4]^{2-}$ is paramagnetic, while $[PtCl_4]^{2-}$ is diamagnetic. For both these complexes, draw the box diagram indicating the distribution of electrons and the type of hybridization involved that explains the observed magnetic behaviour.

(2 marks)

2.7 The crystal field splitting parameter, Δ_O, for some of the chromium complexes is given below. Match the Δ_O values from column **B** with the corresponding chromium complex from column **A**.

A Complex ion	**B** Δ_o (cm^{-1})
i) $[CrF_6]^{3-}$	a) 26,600
ii) $[Cr(H_2O)_6]^{3+}$	b) 22,000
iii) $[CrF_6]^{2-}$	c) 17,400
iv) $[Cr(CN)_6]^{3-}$	d) 15,000

(1.5 marks)

2.8 Determine the oxidation state, coordination number and EAN of the central atom/ion in the following compounds:

a) $[Fe(CN)_6]^{3-}$ b) $Ni(CO)_4$

(3 marks)

2.9 In an octahedral complex, whenever degenerate dx^2-y^2 and dz^2 orbitals are unequally occupied (as is the case with, for example, d^9 ion), the octahedron undergoes distortion. The two d-orbitals then have different energies. This is known as Jahn Teller distortion. This distortion usually occurs by elongation or contraction along z-axis, and the single electron correspondingly occupies highest energy dx^2-y^2 or dz^2 orbital. In a crystal lattice structure of CuF_2, the Cu^{2+} is six coordinate with four F^- at a distance of 1.93 Å and two F^- at 2.27 Å. Draw the relevant crystal field splitting diagram for the distorted octahedral geometry of CuF_2.

a) The tetragonal distortion in the above case is

i) by elongation along z-axis. ☐

ii) by compression along z-axis. ☐

b) The single electron is in

i) dz^2 orbital. ☐

ii) dx^2-y^2 orbital. ☐

(3 marks)

2.10 The order of trans effect in the series of ligands is CN ~CO ~C_2H_4 > PPh_3 > NO_2^- > I^- > Br^- > Cl^- > NH_3 ~ Py > OH^- > H_2O

Draw the structures of the product of the following reactions on the basis of trans effect.

i) $[PtCl_3NH_3]^- + NO_2^- \rightarrow$

A

A + $NO_2^- \rightarrow$

B

ii) $[PtCl(NH_3)_3]^+ + NO_2^- \rightarrow$

C

C + $NO_2^- \rightarrow$

D

(2 marks)

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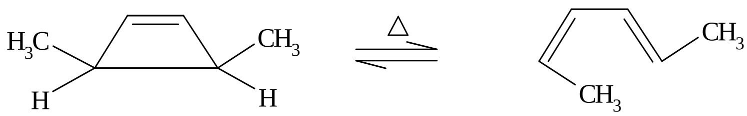
Problem 3 14 marks

Chemistry of isomeric benzenes

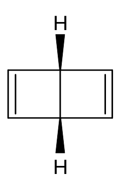
The structure of benzene puzzled chemists for a longtime after its discovery in 1825. Some of the structures proposed for benzene are highly strained cyclic compounds. In the last few decades, organic chemists have synthesized several unusual polycyclic strained compounds. One of the common strategies in such syntheses is to use pericyclic reactions. Pericyclic reactions are the reactions wherein a cyclic shift of electrons in a concerted manner occurs (i.e. bond making and bond breaking take place simultaneously). In such reactions stereochemistry of substituents in the starting compounds plays an important role in deciding the stereochemistry of the products.

A thermal conversion of ***cis*** 3,4-dimethylcyclobutene (**A)** into ***2E, 4Z***-hexadiene **(B)** and vice versa is shown below.



A **B**

Dewar had proposed structure **C** for benzene (Dewar benzene) which consists of two cyclobutene rings fused together.



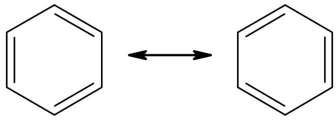
C

3.1 In order to relieve the high strain, **(C)** undergoes thermal rearrangement to form a monocyclic compound **(D)**. Draw the structure of **(D)** with correct stereochemistry and give its IUPAC name with stereodescriptors (E/Z). (Hint: Refer conversion **(A)** → **(B)**).

D

(1.5 marks)

3.2 Interestingly, in spite of high strain, **(C)** does not get transformed spontaneously into Kekule structure (**E**), which is very stable.



E

Treatment of **(C)** with a protic acid results in **(E)**. Suggest a possible mechanism using curved arrow, for this conversion.

(2 marks)

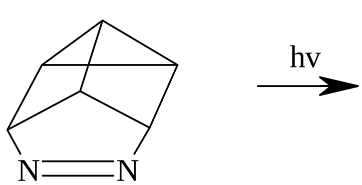
3.3 Lead tetraacetate (LTA) is a reagent used to bring about oxidative decarboxylation of vicinal dicarboxylic acids producing corresponding alkenes. Predict the structure of compound **F** ($C_8H_8O_4$) that would give **(C)** on treatment with LTA.

F

(1 mark)

3.4 Ladenburg also proposed a structure for benzene (Ladenburg benzene), later known as Prismane **H**. It accounted for formation of one mono substitution and three isomeric disubstitution products.

Compound **(G)** on photolysis gives (**H**) in small amount. Draw the structure of (**H**).



(G)

(H)

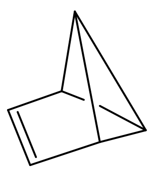
+ N_2

(1 mark)

3.5 Draw the Ladenburg benzene structures of all possible isomeric dibromobenzenes.

(1.5 marks)

Benzvalene **(I)**, (also known as Hückel benzene), was another structure proposed for benzene.



I

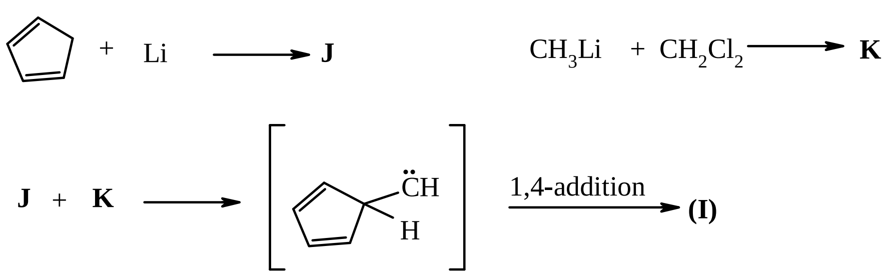
^{1}H-NMR is an important spectroscopic tool to identify hydrogen atoms in different chemical environments. Each type of hydrogen atom gives a separate signal in the spectrum.

3.6 How many peaks are expected in the ^{1}H-NMR spectrum of (**I**)?

(a) Two ☐ (b) Three ☐ (c) Four ☐

(0.5 mark)

3.7 Identify **J** and **K** in the following sequence of reactions in the synthesis of benzvalene (**I**).



J

K

(2 marks)

3.8 Trimethylene cyclopropane **(N)**, is another isomer of benzene. It can be prepared from **L** as follows. Identify **M** and **N**.

L

M

M —NaOEt, EtOH→

N

(2.5 marks)

3.9 Draw the structures of the stereoisomers of **(L)** used in **3.8**.

(1 mark)

3.10 Predict the structure of the adduct **(O)** that would result from the Diels-Alder reaction of **(N)** and acetylene (C_2H_2).

O

(1 mark)

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Problem 4 **10 marks**

s-Block Elements

Alkali and alkaline earth metals (s-block elements) generally occur in minerals and natural water in combined state as halides, sulphates, carbonates, nitrates, silicates etc. The metals are highly electropositive and their compounds are important constituents of biological fluids such as blood.

4.1 Alkali metals are typically soft, show low densities, and have low melting and boiling points. This is because they have

a) only one valence electron ☐

b) large atomic size ☐

c) negative values of standard reduction potentials ☐

d) negligible electron gain enthalpy ☐

(1 mark)

All alkali metals burn in air to form oxides, peroxides and super oxides, depending on the nature of metal and are used in every walk of life. Super oxide of potassium is used in breathing masks for inhalation as well as exhalation.

4.2 Write the balanced chemical equation for the possible reactions of super oxide of potassium during inhalation and exhalation.

Inhalation
Exhalation

(1.5 marks)

4.3 Give the balanced equations for the reaction of lithium and cesium with oxygen.

(1 mark)

4.4 In the vapour state, alkali metals may exist as atoms or diatomic molecules.

If sodium forms a diatomic molecule what will be i) its bond order and

ii) its magnetic behaviour?

i) Bond order

ii) diamagnetic ☐ paramagnetic ☐

ferromagnetic ☐

(1 mark)

4.5 Sodium dissolves in liquid ammonia giving a blue coloured solution. Write chemical equation for this reaction.

(1 mark)

4.6 Mark the correct statement/s applicable to the above solution

a) This solution does not absorb energy in the visible region ☐

b) It is paramagnetic in nature ☐

c) On standing this solution slowly liberates hydrogen resulting in the formation of sodium amide ☐

d) On concentrating, blue colour changes to bronze colour retaining its magnetic behaviour ☐

(1 mark)

4.7 Solid sodium amide, $NaNH_2$ has a cubic closed packed arrangement of NH_2^- ions with ______ voids occupied by Na^+ ions.

a) half the number of octahedral ☐

b) all tetrahedral ☐

c) half the number of tetrahedral ☐

d) double the number of octahedral ☐

(1 mark)

4.8 Metallic sodium is used as a drying agent for

a) chloroform ☐

b) cyclohexane ☐

c) diispropyl ether ☐

d) diethylamine ☐

(1 mark)

4.9 Alkali metals readily react with halogens to form metal halides, MX (X = F, Cl, Br, I), The enthalpy, $\Delta H^o_f(MX)$ will depend upon

a) ionization energy of alkali metal ☐

b) electron gain enthalpy of halogen ☐

c) electronegativity of halogen ☐

d) sizes of cations and anions ☐

(1 mark)

4.10 Lithium halide that is least soluble in water is ☐

(0.5 mark)

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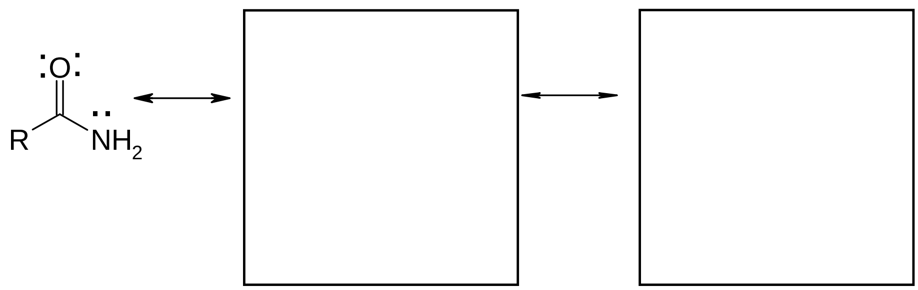
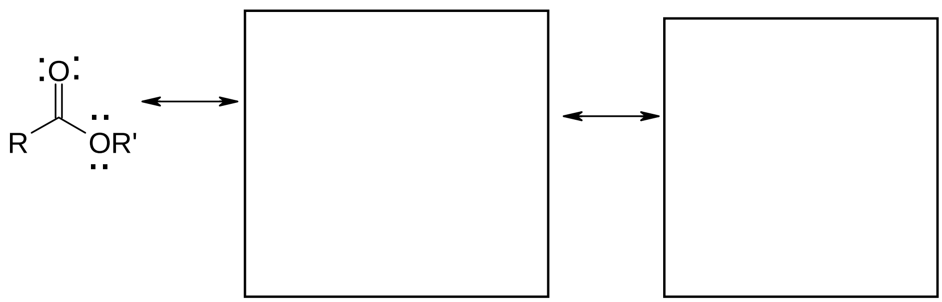
Problem 5 **17 marks**

Carboxylic acid derivatives

Carboxylic acids occur widely in nature. Common carboxylic acid derivatives used as synthons for organic synthesis are acid chlorides, esters and amides. However, reactivities of these species are different.

5.1 Draw the resonance structures (Lewis) of amide and ester.





(2 marks)

5.2 The correct order of resonance stabilization is

(a) Acid Chloride > Amide > Ester

(b) Ester > Amide > Acid Chloride

(c) Amide > Ester > Acid Chloride

(d) Acid Chloride > Ester > Amide

(e) Amide > Acid Chloride > Ester

(f) Ester > Acid Chloride > Amide **(0.5 mark)**

5.3 Oxygen atom of the carbonyl group is most basic in

Amide ☐ Ester ☐ Acid chloride ☐

(1 mark)

In IR spectrum, a carbonyl group shows a peak in the range 1600-1800 cm^{-1}. Stronger is the bond, higher is the absorption value. IR spectra of sample **A** (acetamide), **B** (acetyl chloride) and **C** (ethyl acetate) were recorded.

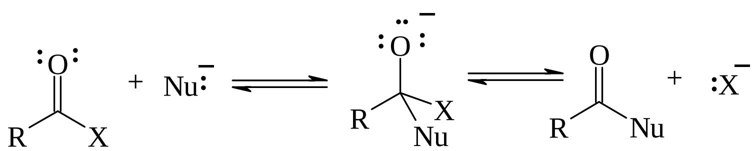
5.4 Match the following IR frequencies with samples **A**, **B** and **C**.

1650 cm^{-1}	
1750 cm^{-1}	
1800 cm^{-1}	

(1 mark)

Acid derivatives (RCOX) undergo nucleophilic reactions at the carbonyl group. The rate of such a reaction depends on the group X.

The reaction proceeds via the following steps.



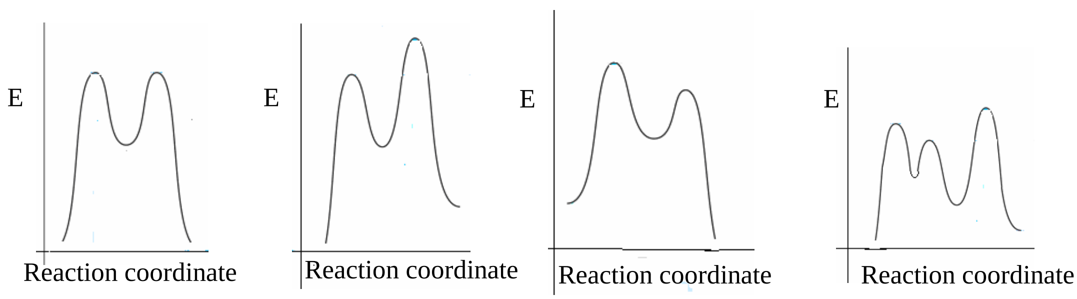
5.5 The compound which would undergo nucleophilic substitution fastest would be

$CH_3CH_2CONH_2$ ☐ $CH_3CH_2COOCH_3$ ☐

CH_3CH_2COCl ☐

(0.5 mark)

Based on the above mechanism, following four probable potential energy diagrams can be drawn.



A **B** **C** **D**

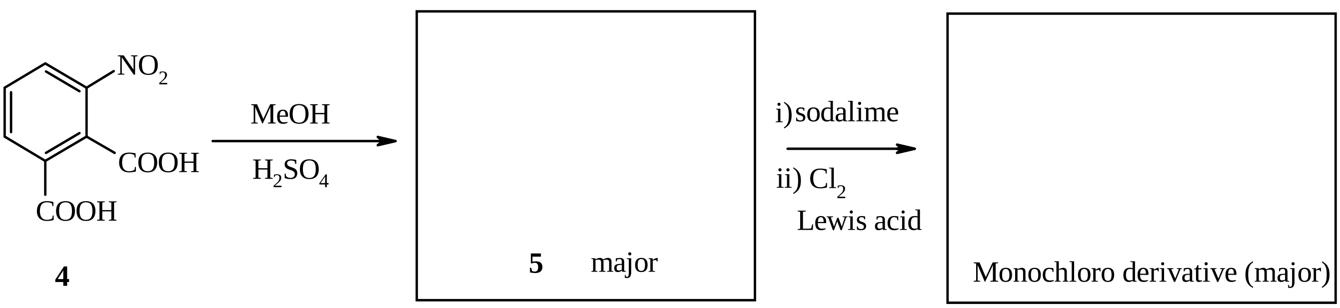
5.6 Identify the potential energy diagrams for the best and the poorest leaving groups among $-NH_2$, $-OC_2H_5$ and $-Cl$

Best ☐ Poorest ☐

(1 mark)

The acid-catalyzed preparation of esters from carboxylic acids is known as Fischer esterification. When 3-nitrophthalic acid **4** is esterified with methanol in the presence of sulfuric acid, ester **5** is obtained. Compound **5** on treatment with soda lime gives a compound which gives one monochloro derivative as the major product on chlorination.

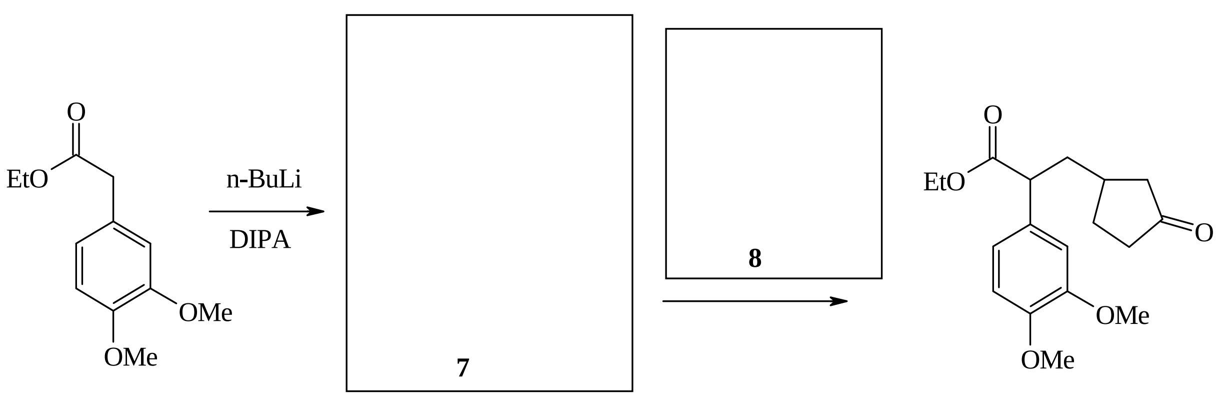
5.7 Give the structure of compound **5** and the monochloro derivative.



(1 mark)

When ester **6** is treated with n-BuLi and diisopropylamine (DIPA), enolate **7** is obtained which on subsequent treatment with compound **8** produces compound **9**.

5.8 Identify compounds 7 and **8**.

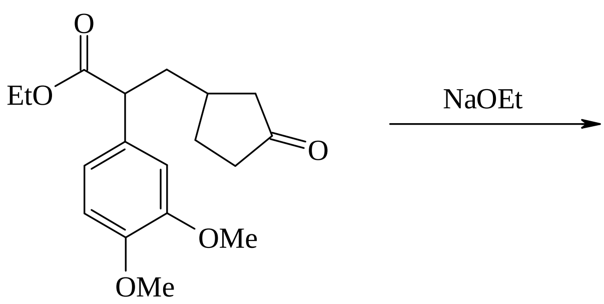


6 **9**

(1 mark)

Enolates undergo further reaction, intramolecularly or intermolecularly with electron defcient carbon atom to form a new C-C bond.

5.9 When compound **9** is treated with sodium ethoxide, a mixture of three products **10**, **11** and **12** is obtained. Predict the structures of the products **10**, **11**, and **12**.



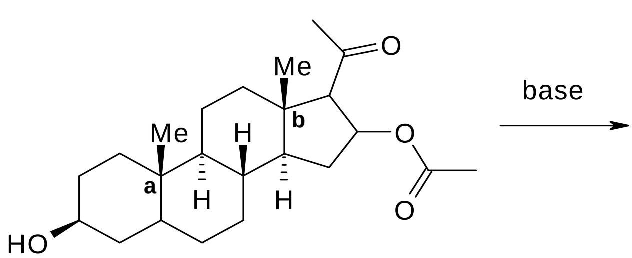
10 + **11** + **12**

9

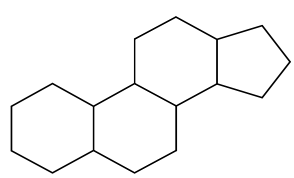
10 + **11** + **12**

(3 marks)

5.10 Steroids is a family of natural products, which usually occur in many biological systems. A steroid **13** when treated with a base, forms a stable compound **14**. Write the structure of the major product (**14)**.



13



14

(0.5 mark)

5.11 (i) The number of stereocenters in **13**, is

(0.5 mark)

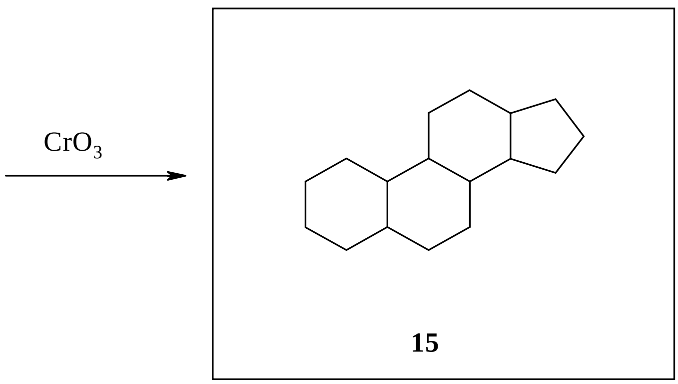
(ii) For compound **13**, the absolute configurations of the carbon centers **a** and **b** are

(1 mark)

When compound **14** is further treated with chromium trioxide, compound **15** is formed.

5.12 Write the structure of compound **15**.

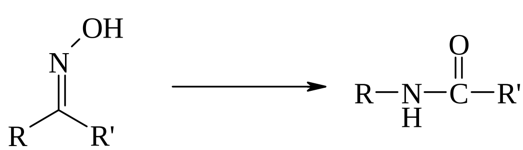
14



15

(0.5 mark)

Oximes of ketones and esters of oximes rearrange on heating or in the presence of an acid to form amides (Beckmann rearrangement).

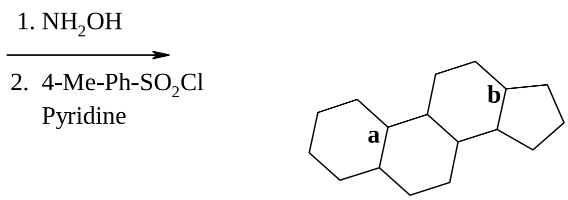


oxime

Beckmann rearrangement

5.13 Compound **15,** on treatment with hydroxylamine hydrochloride and base followed by 4-MePhSO$_2$Cl gives product **16**. Draw the structure of **16**.

15



16

(1 mark)

5.14 On heating compound **16** followed by hydrolysis a mixture of two compounds **17** and **18** is obtained. Write the structures of compounds **17** and **18.**

(Hint: the products contain five membered ring and show strong peaks at 1620 – 1650 cm^{-1}).

17

18

(2.5 marks)

Table 1: Characteristic regions of IR absorptions

Functional Group	Region (cm^{-1})
Hydroxyl	3000 – 4000
Carbonyl	1620 – 1800
Ether	1050 – 1150
Olefin	1580 - 1620

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Problem 6 **17 marks**

Chemical Thermodynamics

Greenhouse gas CO_2 can be converted to CO(g) by the following reaction

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$, termed as water gas reaction.

6.1 Calculate ΔG for the reaction at 1000 K ($\Delta H_{1000\ K}$ = 35040 J mol^{-1} $\Delta S_{1000\ K}$ = 32.11 J mol^{-1} K^{-1}).

(0.5 mark)

6.2 Calculate equilibrium constants Kp and Kc for the water gas reaction at 1000 K (Note: The gases behave ideally.)

(1.5 marks)

6.3 A mixture of gases containing 35 vol. % of H_2, 45 vol. % of CO and 20 vol. % of H_2O is heated to 1000 K. What is the composition of the mixture at equilibrium?

(3.5 marks)

6.4 Calculate ΔH at 1400 K, using the given data for 1000 K, assuming the C^o_p values remain constant in the given temperature range.

$\Delta H = 35040\ J mol^{-1}$; $C^o_p(CO_2) = (42.31 + 10.09 \times 10^{-3}\ T)\ J\ mol^{-1}\ K^{-1}$

$C^o_p(H_2) = (27.40 + 3.20 \times 10^{-3}\ T)\ J\ mol^{-1}\ K^{-1}$

$C^o_p(CO) = (28.34 + 4.14 \times 10^{-3}\ T)\ J\ mol^{-1}\ K^{-1}$

$C^o_p(H_2O) = (30.09 + 10.67 \times 10^{-3}\ T)\ J\ mol^{-1}\ K^{-1}$

(2 marks)

6.5 Based on your answer in **6.4,** mark the correct box:

a) Kp will increase with increase in temperature ☐

b) Kp will not change with increase in temperature ☐

c) Kp will decrease with increase in temperature ☐

(0.5 mark)

B. Fuel combustion in automobiles

Carbon monoxide emitted by automobiles is an environmental hazard. A car has an engine of four cylinders with a total cylinder volume of 1600cc and a fuel consumption of 7.0 dm^3 per 100 km, when driving at an average speed of 80 km/hr. In one second, each cylinder goes through 25 burn cycles and consumes 0.400 g of fuel. The compression ratio, which is the ratio between the smallest and largest volume within the cylinder as the piston moves forward and backward is 1:8.

6.6 Calculate the air intake of the engine (m^3s^{-1}), if the gaseous fuel and air are introduced into the cylinder when its volume is largest until the pressure is 101.0 kPa. The temperature of both incoming air and fuel is 100 °C. (Assume the fuel to be isooctane, C_8H_{18})

(3 marks)

Air contains 21.0 % of O_2 and 79.0 % of N_2 (by volume). It is assumed that 10.0 % of the carbon of the fuel forms CO upon combustion and that N_2 in air remains inert.

6.7 The gasified fuel and air are compressed to their lowest volume and then ignited.

The overall stoichiometric equation for the combustion reaction is

$C_8H_{18} + 12.1O_2 \rightarrow 0.8\ CO + 7.2\ CO_2 + 9\ H_2O$

Calculate the temperatures of the

i) gases just at the time of maximum compression, and

ii) exhaust gases leaving the cylinder if the final pressure in the cylinder is 200 kpa.

Relevant data needed for one burn cycle is given below:

Compound	**ΔH_f (kJ mol^{-1})**	**Cp (J mol^{-1} K^{-1})**	**Composition of gases after combustion (Mol $\times 10^{-4}$)**
N_2 (g)	0.0	29.13	101.91
O_2 (g)	0.0	29.36	10.10
CO (g)	-110.53	29.14	1.12
CO_2 (g)	-395.51	37.11	10.11
H_2O (g)	-241.82	33.58	12.36
Isooctane	-187.82		

(2.5 marks)

6.8 To convert CO(g) into CO_2(g) the exhaust gases are led through a bed of catalysts with the following work function:

$$\left(\frac{n(CO)}{n(CO_2)}\right) = \frac{1}{4} \times k \left(\frac{n(CO)}{n(CO_2)}\right)_i \times v \times e^{-\left(T/T_0\right)}$$

where, [n(CO) / n(CO_2)] is the molar ratio of CO and CO_2 leaving the catalyst bed, [n(CO) / n(CO_2)]$_i$ is the molar ratio before entering the catalyst bed, v is the flow rate in mol s^{-1} and T the temperature of the exhaust gases. T_0 is a reference temperature (373 K) and k is 3.141 s mol^{-1}. Calculate the molar composition of the exhaust gases leaving the catalyst bed.

(3.5 marks)

Name of Student	**Roll no.**

Problem 7 **10 marks**

Vinegar is an acid with its key ingredient, acetic acid. It is widely used for food preservation and cooking. The acetic acid concentration for table vinegar is typically 5% whereas higher concentration upto 18% is used as preservative. The word "vinegar" is derived from *vin aigre*, meaning "sour wine".

A table vinegar sample contains 5% (mass/mass) of acetic acid.

7.1 To what volume 10 mL of the above sample should be diluted to prepare 0.10 M acetic acid solution. (density 1.05 g mL^{-1} , Molar mass of CH_3COOH – 60.0 g mol^{-1})

(1 mark)

7.2 Write balanced equation for the dissociation of acetic acid [CH_3COOH] in the above solution and give an appropriate expression for equilibrium constant Ka.

(1mark)

7.3 For the diluted solution, write the appropriate expression for total concentration of acetic acid expressed as C_T. Derive the exact expression for $[H_3O^+]$ in terms of Ka and C_T.

(1.5 marks)

7.4 Apply appropriate approximation to simplify the expression for $[H_3O^+]$ written by you in **7.3** and calculate the pH of the diluted vinegar solution. (Ka= 1.75×10^{-5})

(1.5 marks)

7.5 5.0 mL of 0.1 M NaOH solution is added to 50 mL of the 0.1 M acetic acid solution

a) Write the equilibrium reactions for dissociated and undissociated acetic acid present in the above solution.

b) For the above system, write appropriate expressions for $[CH_3COOH]_{eq}$ and $[CH_3COO^-]_{eq}$. (hint: the expressions should have $[H_3O^+]$, $[OH^-]$, C_T and $[CH_3COONa]$).

c) Apply appropriate approximation and get the simplified expression for $[H_3O^+]$.

d) Calculate the pH of the resulting acetic acid solution

(4 marks)

7.6 Calculate the pH when 50 mL of 0.1 M NaOH is added to 50 mL of 0.1 M acetic acid solution. ($K_w = 1.00 \times 10^{-14}$)

(1 mark)

Equivalent solutions may exist

Problem 1 17 marks

Thermal and photolytic decomposition of Acetaldehyde

1.1 a)

$$-\frac{d[CH_3CHO]}{dt} = k[CH_3CHO]^{3/2}$$

$$\frac{d[CH_4]}{dt} = \frac{d[CO]}{dt} = k[CH_3CHO]^{3/2}$$

(b)

Order = 3/2

Rate = 8 v

1.2

CH_4, CD_4 and CO

1.3 (a)

Propogation steps : (ii) and (iii)

Termination step: (iv)

(b)

$$[\bullet CH_3] = \left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^{1/2}$$

$$[\bullet CH_3CO] = \frac{k_2}{k_3}\left(\frac{k_1}{2k_4}\right)^{1/2} [CH_3CHO]^{3/2}$$

(c)

$$\frac{d[CO]}{dt} = k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

1.4 (a)

$CH_3CHO + h\nu \rightarrow \bullet CH_3 + \bullet CHO$
Rate = I_{abs}

$[\bullet CH_3] = (I_{abs}/2k_4)^{1/2}\,[CH_3CHO]^{3/2}$

$d[CO]/dt = k_2 \times (I_{abs}/2k_4)^{1/2}\,[CH_3CHO]^{3/2}$

(b)

λ = 317.5 nm

1.5 (a)

$$E_{thermal} = E_2 + \frac{1}{2}(E_1 - E_4)$$

(b)

$E_{photochemical} = E_2 - \frac{1}{2} E_4$

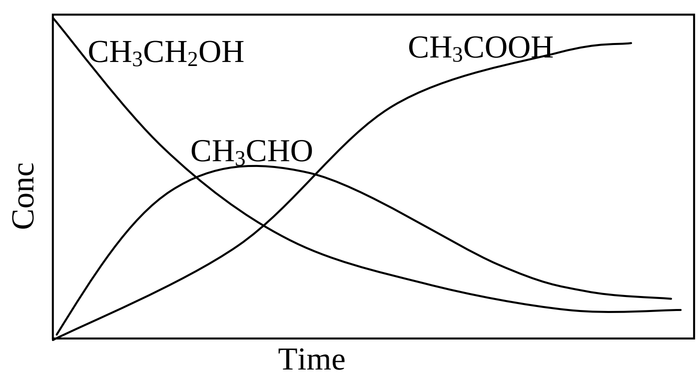
1.6 (a)

$E_{thermal}$ = 196.46 kJ mol^{-1}

(b)

5.879×10^{-4} mol dm^{-3} sec^{-1}

1.7 (a)



(b)

$[CH_3CHO] = k_5/k_6\,[CH_3CH_2OH]$

Problem 2 19 marks

Chemistry of coordination compounds

2.1

$CuSO_4 + 6H_2O \rightarrow [Cu(H_2O)_6]^{2+} + SO_4^{2-}$

White — Blue solution

or balanced equation with $[Cu(H_2O)_4]^{2+}$ entity

$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$

$2OH^-$ from dil NH_3; $Cu(OH)_2$ Blue ppt.

$Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$

$[Cu(NH_3)_4]^{2+}$ Deep blue soln

2.2

b] completely filled d-level in Cu(I)

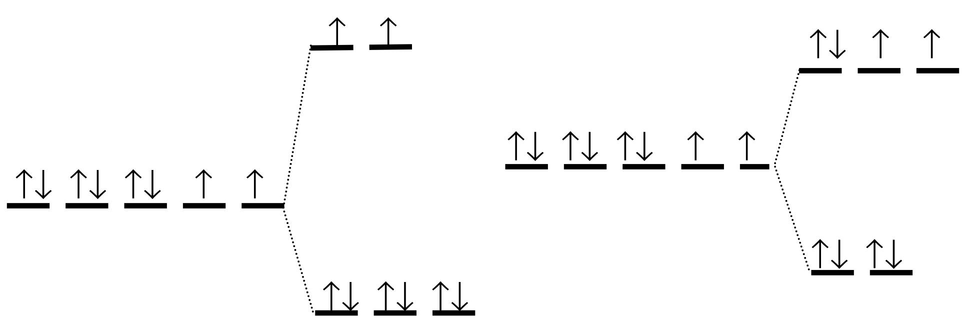
2.3

a] oxidation state of the metal.

b] nature of the ligand.

c] geometry of the complex.

2.4



$[Ni(H_2O)_6]^{2+}$ $[NiCl_4]^{2-}$

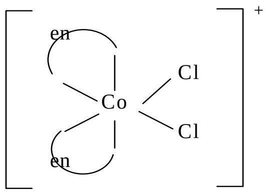
$[Ni(H_2O)_6]^{2+}$ is octahedral.

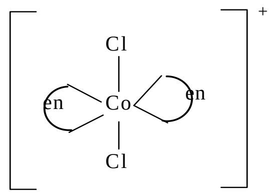
$[NiCl_4]^{2-}$ is tetrahedral

2.5

a] . IUPAC Name : Dichlorobis(ethylenediamine)cobalt(III) ion.
Dichlorobis(ethane-1,2-diamine)cobalt(III) ion
Dichloridobis(ethylenediamine)cobalt(III) ion.
Dichloridobis(ethane-1,2-diamine)cobalt(III) ion

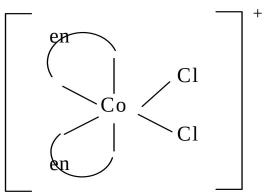
b]. Geometrical isomers:

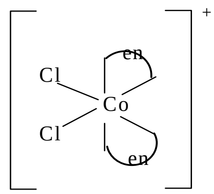




c] cis-$[CoCl_2(en)_2]^+$ is optically active.

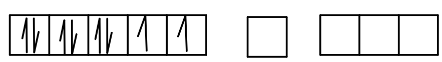
d] Two optical isomers of cis-$[CoCl_2(en)_2]^+$:



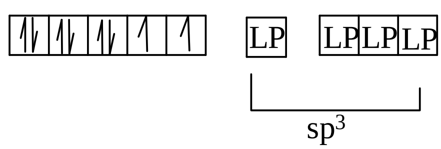


2.6

Ni^{2+} [Ar] $3d^8$

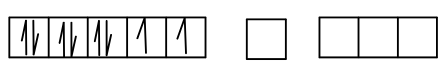


$[NiCl_4]^{2-}$

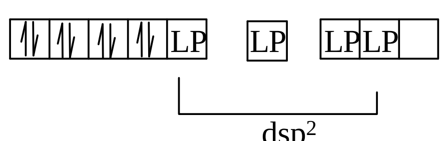


T sp^3 hybridization
etrahedral
Paramagnetic (2 unpaired electrons)

Pt^{2+} [Xe] $5d^8$



$[PtCl_4]^{2-}$



dsp^2 hybridization
Square planar
Diamagnetic (no unpaired electrons)

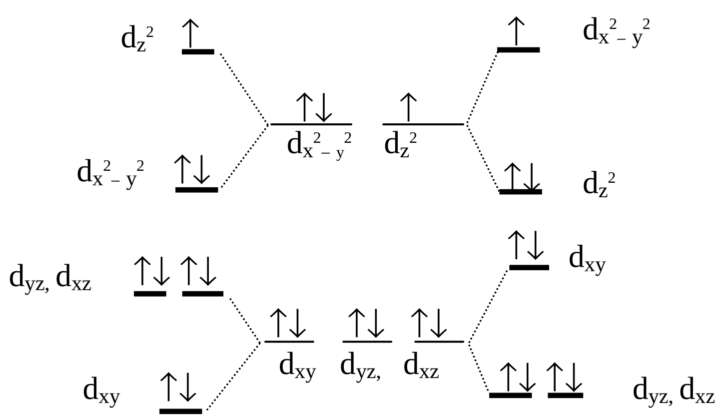
2.7

A		B Δ_o (cm^{-1})
i) $[CrF_6]^{3-}$		d) 15,000
ii) $[Cr(H_2O)_6]^{3+}$		c) 17,400
iii) $[CrF_6]^{2-}$		b) 22,000
iv) $[Cr(CN)_6]^{3-}$		a) 26,600

2.8

Answer:	a) $[Fe(CN)_6]^{3-}$	b) $Ni(CO)_4$
Oxidation state	Fe(III)	Ni(0)
Coordination No.	of Fe(III) : 6	of Ni(II) : 4
EAN of central metal ion	35	36

2.9

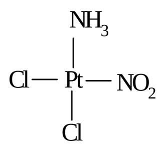


Tetragonally distorted octahedron contraction along z-axis | octahedron | Tetragonally distorted octahedron elongation along z-axis

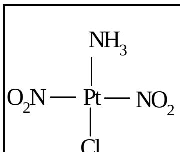
a) (i) by elongation along z-axis.

b) (ii) dx^2-y^2 orbital.

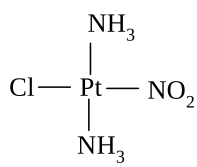
2.10



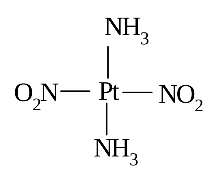
A



B



C



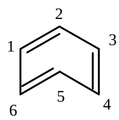
D

Problem 3 14 marks

Chemistry of isomeric benzenes

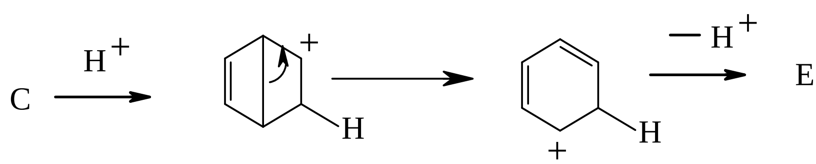
3.1

Z,Z,E -1,3,5-cyclohexatriene

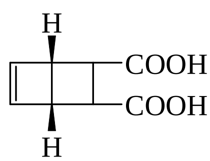


(D)

3.2

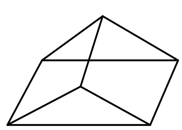


3.3



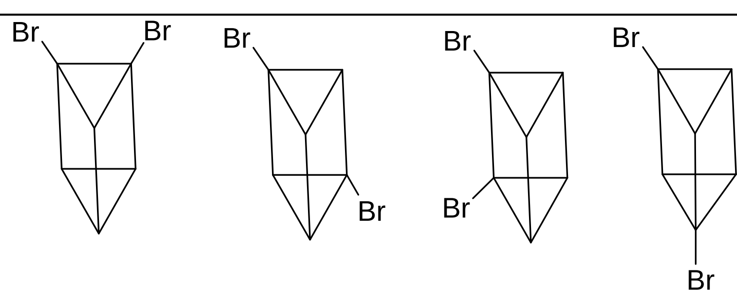
F

3.4



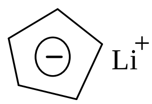
H

3.5



3.6 (b) Three X

3.7

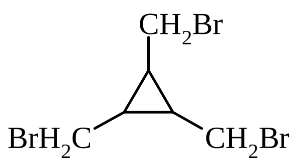


J

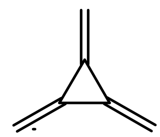
$\ddot{C}HCl$

K

3.8

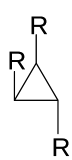


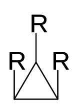
M



N

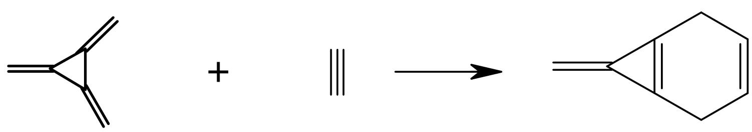
3.9





R=COOEt

3.10



N **O**

Problem 4 10 marks

s-Block Elements

4.1 a) only one valence electron [X]

b) large atomic size [X]

4.2

Inhalation		$2\ KO_2 + 2\ H_2O \rightarrow 2\ KOH + H_2O_2 + O_2$
Exhalation		$KOH + CO_2 \rightarrow KHCO_3$
	or	$4\ KO_2 + 2\ CO_2 \rightarrow 2K_2\ CO_3 + 3O_2$
	or	$2KOH + CO_2 \rightarrow K_2\ CO_3 + H_2O$

4.3

I $4\ Li + O_2 \rightarrow 2\ Li_2O$

II $Cs + O_2 \rightarrow CsO_2$

4.4

i) Bond order = 1

ii) diamagnetic [X]

4.5

$Na + (x + y)\ NH_3 \rightarrow [Na(NH_3)_x]^+ + [e(NH_3)_y]^-$

OR

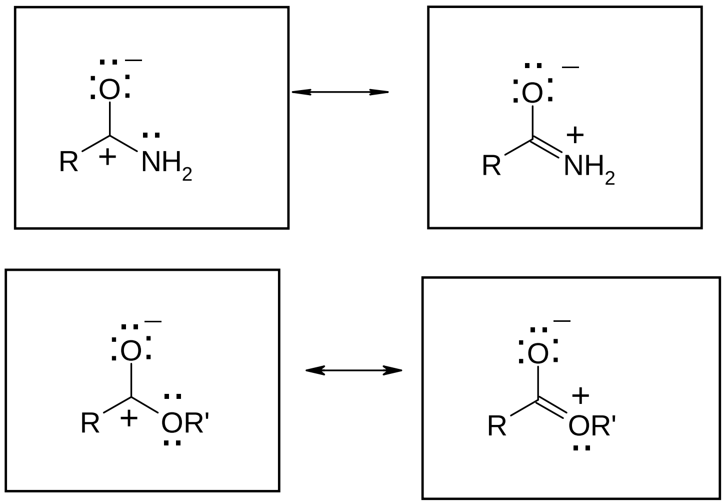
$Na + NH_3 \rightarrow Na^+ + e^-_{\text{solvated / (am)}}$

4.6	b) It is paramagnetic in nature	X
	c) On standing this solution slowly liberates hydrogen resulting in the formation of sodium amide	X
4.7	c) half the number of tetrahedral	X
4.8	b) cyclohexane	X
	c) diisopropyl ether	X
4.9	a) ionization energy of alkali metal	X
	b) electron gain enthalpy of halogen	X
	d) sizes of cations and anions	X
4.10	LiF	

Problem 5 17 marks

Carboxylic acid derivatives

5.1



5.2 (c) Amide > Ester > Acid Chloride | X |

5.3 Amide | X |

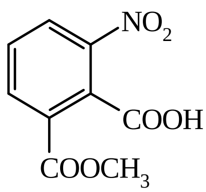
5.4

1650 cm^{-1}	A
1750 cm^{-1}	C
1800 cm^{-1}	B

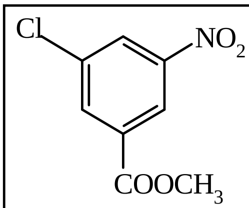
5.5 CH_3CH_2COCl | X |

5.6 Best | C | Poorest | B |

5.7

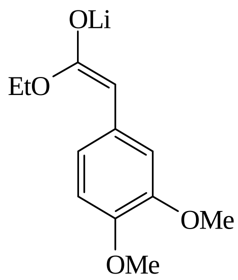


5 major



Monochloro derivative (major)

5.8



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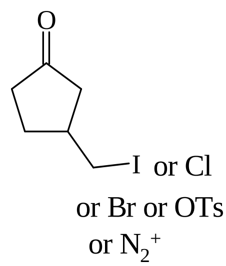

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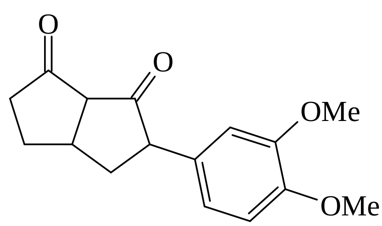
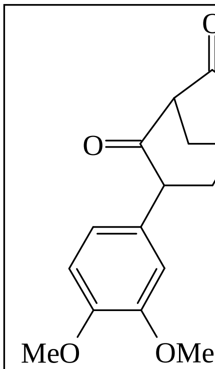
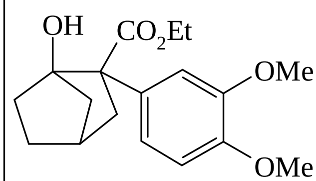
5.9

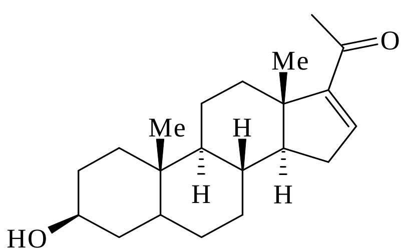






10 **11** **12**

5.10

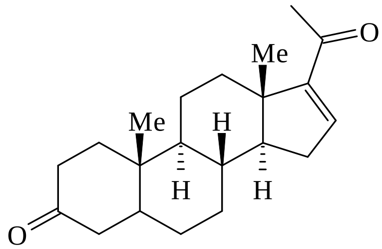


14

5.11 (i) 9

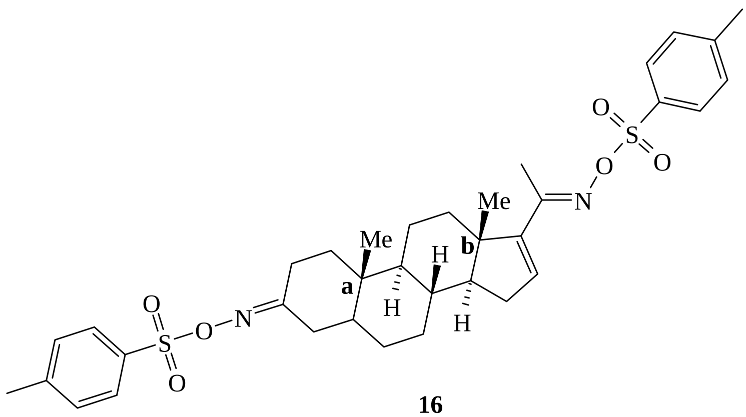
(ii) Both are S

5.12



15

5.13



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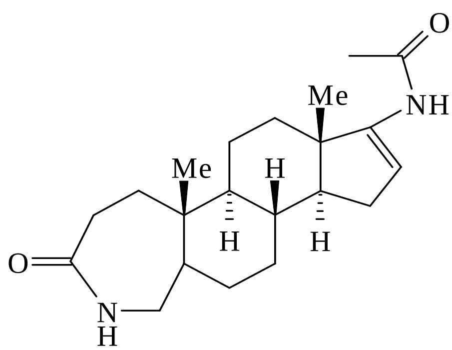
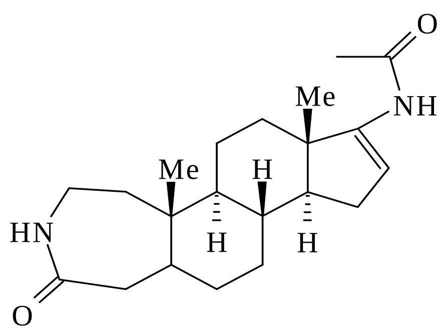
5.14



17



18

Problem 6 17 marks

Chemical Thermodynamics

6.1

2930 J

6.2

Kp = 0.7030

Kp = Kc

6.3

$X_{CO} = 0.342$, $X_{H_2} = 0.458$, $X_{H_2O} = 0.092$, $X_{CO_2} = 0.108$

$X_{CO} = 34.95\%$, $X_{H_2} = 45.41\%$, $X_{H_2O} = 9.59\%$, $X_{CO_2} = 10.06\%$

6.4

$\Delta H_{1400} = 31258$ J

6.5 a) Kp will increase with increase in temperature X

6.6

Air intake (engine;m^3s^{-1}) = $V_A = 4 \times 9.902 \times 10^{-3}\ m^3s^{-1} = 0.0396\ m^3s^{-1}$

6.7

$T_1 = 2060K$

$T_2 = 708\ K$

6.8

Compound	**Molar composition of gases after leaving the bed (Mol $\times 10^{-4}$)**
N_2 (g)	407.64
O_2 (g)	38.55
CO (g)	0.78
CO_2 (g)	44.14
H_2O (g)	49.44

Problem 7 **10 marks**

7.1

V= 87.5 mL

7.2

$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

$Ka = [H_3O^+][CH_3COO^-]/[CH_3COOH]$

7.3

$$[H_3O^+] = -\frac{Ka \pm \sqrt{Ka^2 + 4KaC_T}}{2}$$

7.4

pH = 2.88

7.5 a)

$$CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+$$
$$CH_3COO^- + H_2O \leftrightarrow OH^- + CH_3COOH$$

b)

$$[CH_3COOH]_{eq} = C_T - [H_3O^+] + [OH^-]$$
$$[CH_3COO^-]_{eq} = [CH_3COONa] + [H_3O^+] - [OH^-]$$

c)

$$[H_3O^+] = Ka\frac{C_T}{[CH_3COONa]}$$

d)

pH = 3.80

7.6

pH = 8.73