

Instructions for students

- Write your name and centre at the top of the first pages of all problems.
- This examination paper consists of 40 pages of problems including answer boxes.
- You have 4 hours to complete all the problems.
- All results must be written in the appropriate boxes on the pages. Anything written elsewhere will not be marked. If you need any more sheets for rough work, ask the supervisor.
- You must show the main steps in a calculation in the answer box provided.
- Do not leave the examination room until you are directed to do so.
- Use only non-programmable scientific calculator.
- Values of some fundamental constants are given on page 2.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.

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Some Useful Information

| | |
|-------------------------|---|
| Avogadro's constant | $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ |
| Electronic charge | $e = 1.602 \times 10^{-19} \text{ C}$ |
| Molar gas constant | $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$ $= 8.314 \text{ K Pa}\cdot\text{dm}^3 \text{ K}^{-1}\text{mol}^{-1}$ |
| 1 atomic mass unit (1u) | $= 931.5 \text{ MeV}/c^2$ |
| 1 Dalton | $= 1.661 \times 10^{-27} \text{ kg}$ |
| 1 eV | $= 1.602 \times 10^{-19} \text{ J}$ |
| Mass of electron | $m_e = 9.109 \times 10^{-31} \text{ kg}$ |
| Planck's constant | $h = 6.625 \times 10^{-34} \text{ Js}$ |
| Speed of light | $c = 2.998 \times 10^8 \text{ ms}^{-1}$ |

Problem 1

13 Marks

Potential energy curves and molecular orbitals

J. G. Dojahn, E. M. C. Chen and W.E. Wentworth [J. Phys. Chem. **100**, 9649 (1996)] examined the potential energy diagrams of X_2 and X_2^- where X is a halogen.

The diagram for F_2 and F_2^- is reproduced on the next page.

- 1.1** From this diagram, the dissociation energies (in eV) of F_2 and F_2^- are (Mark **X** in the correct box)

| | | | | | | | | | | | |
|----------------|-----|-----|-----|-----|-----|-----------------------------|-----|-----|-----|-----|-----|
| F ₂ | 1.2 | 1.3 | 1.6 | 1.8 | 1.9 | F ₂ ⁻ | 1.1 | 1.3 | 1.5 | 1.6 | 1.7 |
| | | | | | | | | | | | |

(1 mark)

- 1.2** Using this diagram, the electron affinities of the fluorine atom and F_2 molecule can be calculated. Mark **X** in the correct box for the values (in eV) given below.

| | | | | | |
|--------|-----|-----|-----|-----|-----|
| F atom | 3.2 | 3.4 | 3.6 | 3.7 | 3.8 |
| | | | | | |

| | | | | | |
|-------------------------|-----|-----|-----|-----|-----|
| F ₂ molecule | 2.8 | 3.0 | 3.2 | 3.3 | 3.4 |
| | | | | | |

(2 marks)

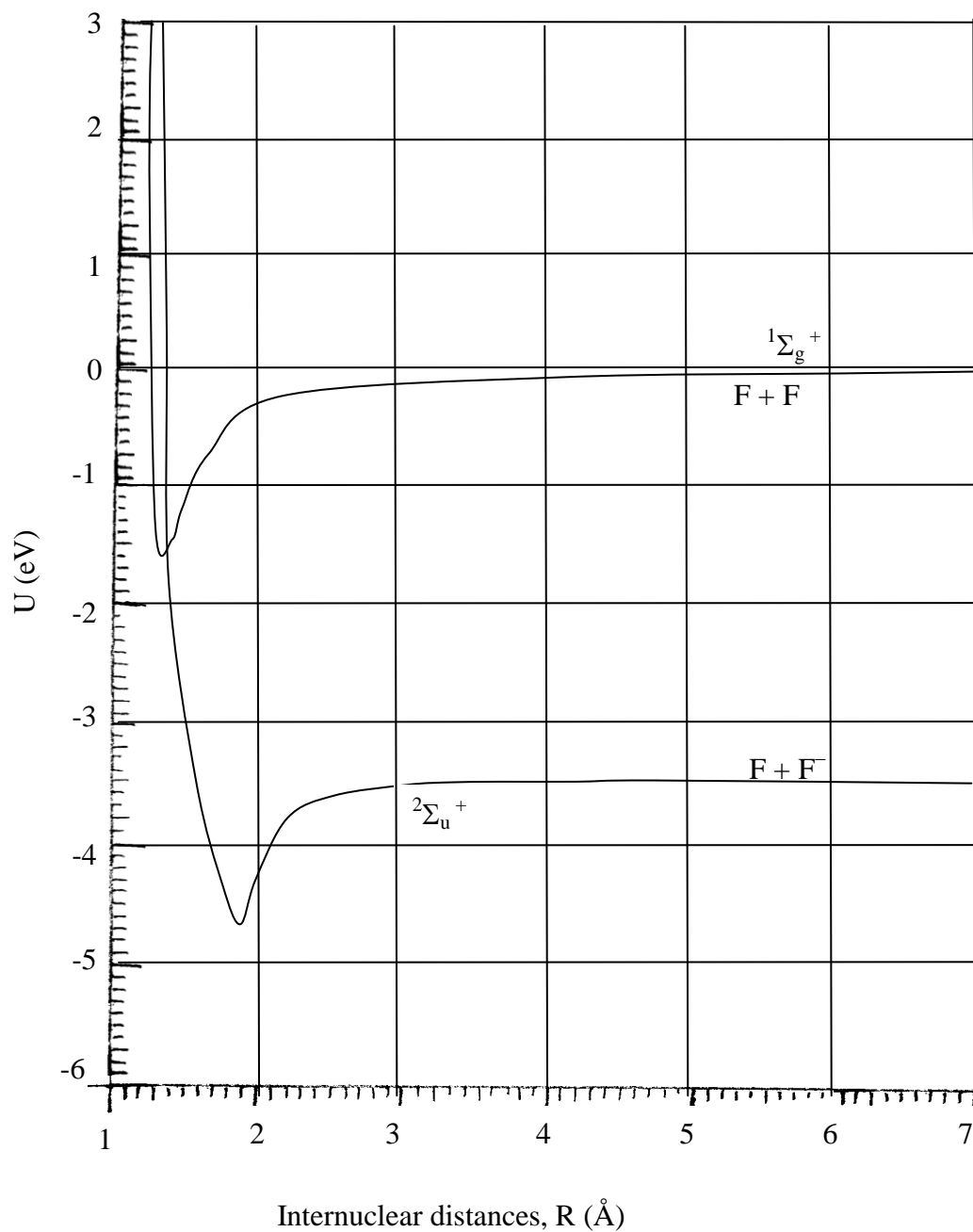
- 1.3** What are the appropriate equilibrium internuclear distances for F_2 and F_2^- ? (choose from the following values : 1.2, 1.4 , 1.6, 1.7, 1.9 and 2.1 Å)

F₂:

F₂⁻:

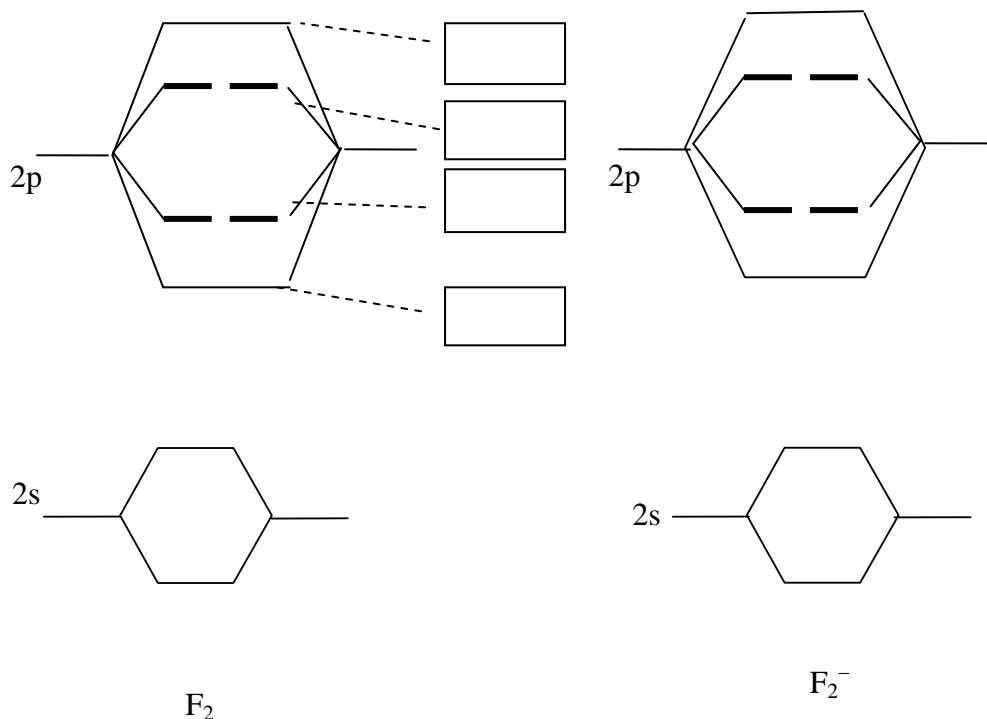
(1 mark)

- 1.4** The vibrational frequencies for F_2 and F_2^- reported by Dojahn *et al.* on fitting the potential energy curves were 917 and 450 cm⁻¹. What is the ratio of the corresponding force constants? **(2 marks)**



The above observation regarding the force constants can be qualitatively explained on the basis of MO theory.

1.5 Fill in the appropriate number of electrons (as \uparrow and \downarrow) in the figure below and label the MO's in the boxes provided.



Choose the labels from the list: π_{2p} , π_{2p}^* , σ_{2p} , σ_{2p}^* , σ_{2s} and σ_{2s}^*

(2 marks)

1.6 The bond orders in F_2 and F_2^- are respectively



(1 mark)

1.7 On the basis of qualitative MO theory, predict the paramagnetic species from the following list (Mark **X** in the correct box/es)



(2 marks)

1.8 The valence photoelectron spectrum of F_2 was measured by A.W. Potts and W.C. Price with the X-ray photon of energy 21.2 eV. In this spectrum two broad peaks corresponding to the electronic kinetic energies of approximately 2.3 and 5.6 eV were seen. What are the corresponding ionization energies I_1 and I_2 ? (1 mark)

1.9 These ionization potentials can be identified as the negative of the respective MO energies, viz $I = -\epsilon$. Write down the labels of MO's that correspond to I_1 and I_2

(refer to 1.5)

I_1 : MO label

I_2 : MO label

(1 mark)

Problem 2

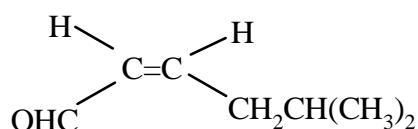
19 Marks

Unsaturated compounds

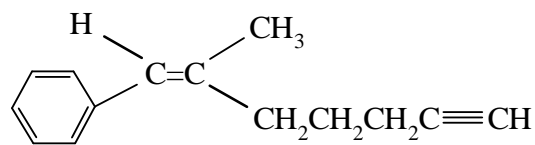
Alkenes and alkynes are collectively referred to as unsaturated compounds, as they contain less hydrogen atoms compared to the corresponding alkanes. Alkenes are also called *olefins*, a term derived from *olefiant gas*, meaning *oil forming gas*. This term originated due to the oily appearance of alkene derivatives. Compared to alkenes, alkynes are not so common in nature, but some plants use alkynes to protect themselves against diseases or predators.

2.1 Give the IUPAC names with stereochemical descriptors (E/Z) for each of the following compounds.

a)

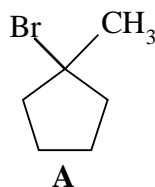


b)



(2 marks)

2.2 The following compound **A** can be prepared by the addition of **HBr** to either of two alkenes **B** and **C**. Give the structures of **B** and **C**.

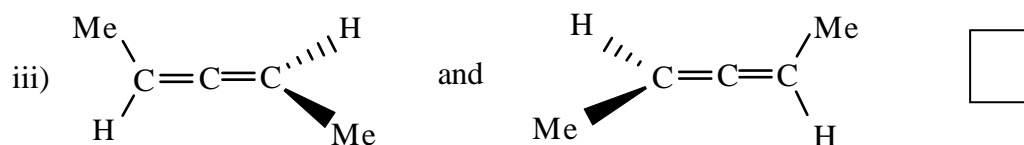
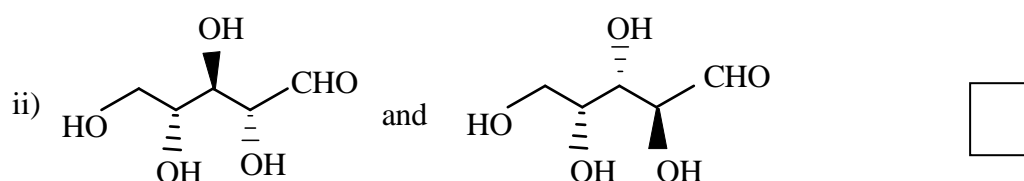
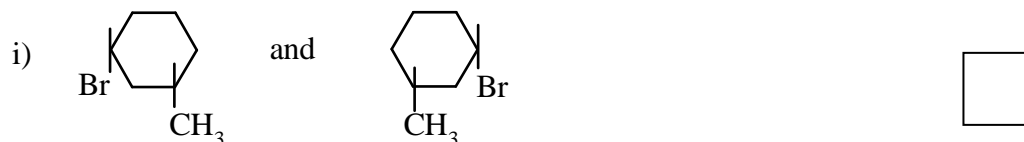


A

(1 mark)

2.3 Draw the energy profile diagram of the reaction of HBr with either **B** or **C** in question 2.2. Label the intermediate/s and transition state/s. (2 marks)

2.4 Indicate the relationship between the compounds in each of the following pairs, as homomers (**H**), enantiomers (**E**) or diastereomers (**D**). Write the corresponding alphabet in the box.



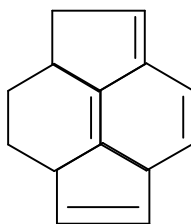
(1.5 marks)

2.5 Heats of hydrogenation indicates the relative stability of alkenes. Match the list of compounds given in **column A** with the corresponding heats of hydrogenation listed in **column B**

| Column A | Column B (kcal mol ⁻¹) |
|---|------------------------------------|
| a) CH ₂ =CHCH ₂ CH=CH ₂ | i) - 226 |
| b) CH ₃ -CH=C=CHCH ₃ | ii) -119 |
| c) CH ₂ =C(CH ₃)-CH ₂ CH ₃ | iii) -295 |
| d) CH ₃ -C(CH ₃)=CHCH ₃ | iv) -252 |
| e) CH ₂ =CH-CH=CHCH ₃ | v) -113 |

(2.5 marks)

- 2.6 Draw the structure of the product/s formed when the following compound is subjected to ozonolysis.



(1 mark)

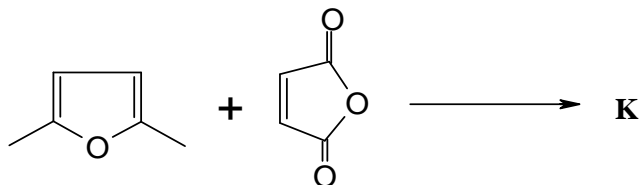
- 2.7 An optically active alkyne **D** has 89.52% carbon. Compound **D** can be catalytically hydrogenated to n-butylcyclohexane. Treatment of **D** with C_2H_5MgBr liberates no gas. Catalytic hydrogenation of **D** over Pd/C in the presence of quinoline (a catalyst poison) and treatment of the product with ozone and then H_2O_2 gives an optically active tricarboxylic acid **E** ($C_8H_{12}O_6$). Compound **E** on heating undergoes dehydration by loss of a molecule of water to give **F**. Draw the possible structures of **D**, **E** and **F**.

(3 marks)

- 2.8 When equimolar amounts of 1,3-butadiene and bromine are reacted at high temperature, two compounds **G** (major) and **H** (minor) with the formula $C_4H_6Br_2$ are formed. Compound **G** reacts with more Br_2 to form compound **I** ($C_4H_6Br_4$) which proved to be a meso compound. Compound **H** reacts with more Br_2 to form both **I** and a diastereomer **J**. Draw the structures of **G** and **H**. Draw the Fischer projection for **I** and **J** indicating the stereochemistry (with R/S designation) of the chiral carbons.

(4 marks)

- 2.9 Diels-Alder reaction of 2,5-dimethylfuran and maleic anhydride gives compound **K** which can exist in two stereoisomeric forms. Draw the structures of the two isomers.



(1mark)

- 2.10 Compound **K** undergoes acid catalysed dehydration to give **L** ($C_{10}H_8O_3$). Draw the structure of **L**.

(1 mark)

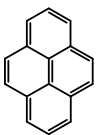
Problem 3

15 Marks

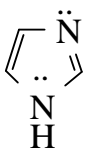
Aromatic compounds

In 1825, Michael Faraday isolated benzene for the first time from the oily mixture that condensed from illuminating gas (the fuel burnt in gas lights). Subsequently many compounds related to benzene were discovered. These compounds had typical odours (*aroma*) and hence this group of compounds was called **aromatic**.

3.1 As per the Hückel's rule of aromaticity, a cyclic compound is aromatic if it is conjugated, planar and has $(4n+2)\pi$ electrons, where, n is a positive integer, including zero. Similar compounds possessing $(4n)\pi$ electrons are highly unstable and are called antiaromatic compounds. It is interesting that compounds adjust their 3D and electronic structures to lower their energies. Answer the following by marking **X** in the correct box.


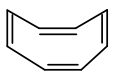
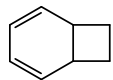
i) Compound  is

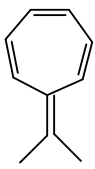
| | |
|---------------------|--------------------------|
| Aromatic | <input type="checkbox"/> |
| Antiaromatic | <input type="checkbox"/> |
| Nonaromatic | <input type="checkbox"/> |

ii) Compound  is

| | |
|---------------------|--------------------------|
| Aromatic | <input type="checkbox"/> |
| Antiaromatic | <input type="checkbox"/> |
| Nonaromatic | <input type="checkbox"/> |

iii) The preferred structure of cyclooctatetraene is

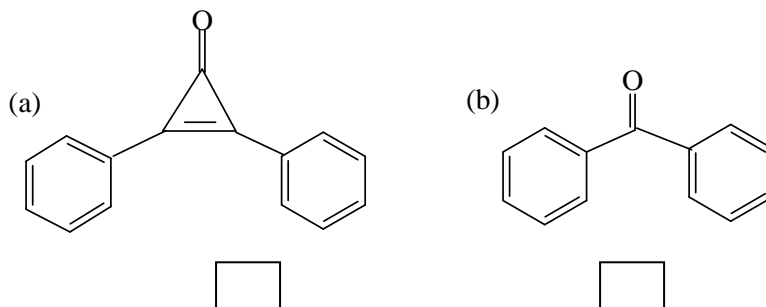
| | |
|--|--------------------------|
|  | <input type="checkbox"/> |
|  | <input type="checkbox"/> |
|  | <input type="checkbox"/> |

iv)  has dipole moment

| | | | |
|------------|--------------------------|-----------|--------------------------|
| Yes | <input type="checkbox"/> | No | <input type="checkbox"/> |
|------------|--------------------------|-----------|--------------------------|

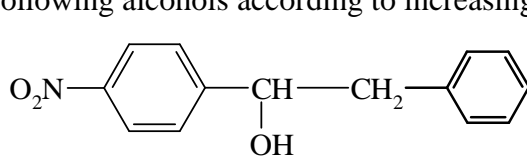


(vi) The compound having higher dipole moment is

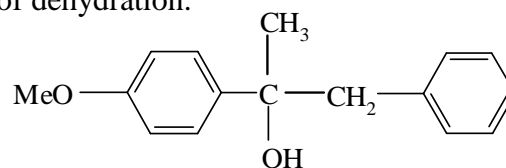


(3 marks)

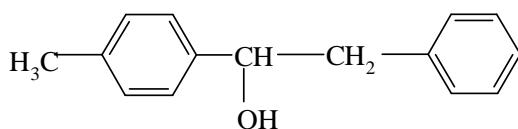
3.2 Alcohols dehydrate to alkenes, which is an acid catalyzed reaction. Arrange the following alcohols according to increasing rate of dehydration.



(I)



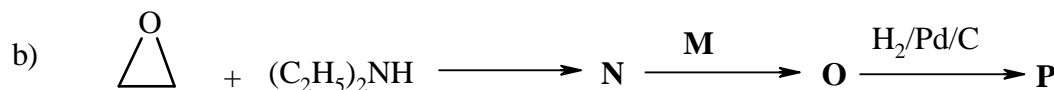
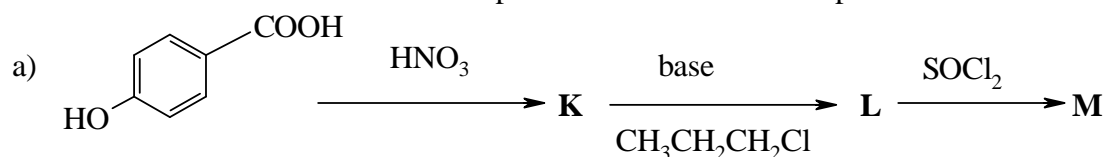
(II)



(III)

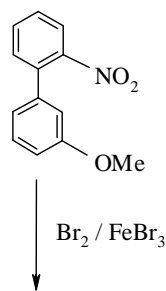
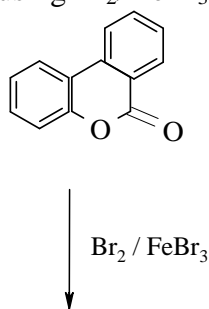
(1 mark)

3.3 The local anesthetic *proparacaine* is synthesized by the following sequence of reactions. Deduce the structure of the product formed at each step.



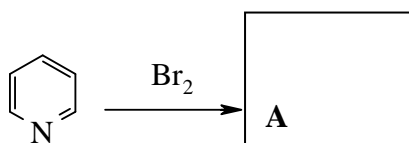
(5 marks)

- 3.4 Draw the structure of the **major** product of bromination of the following compounds using $\text{Br}_2/\text{FeBr}_3$

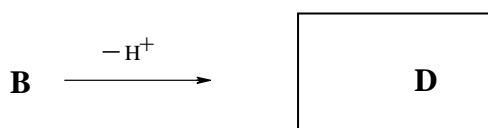
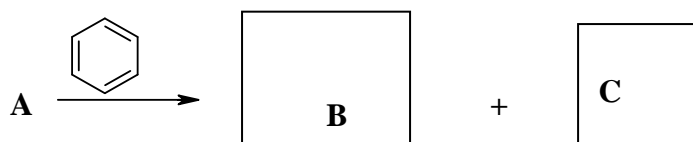


(1.5 marks)

- 3.5 Normally benzene undergoes bromination only in the presence of a Lewis acid. However, bromination of benzene can also be brought about by addition of a small amount of pyridine (**Q**). **Q** catalyses the reaction by involving the lone pair of electrons on nitrogen. This is an example of 'nucleophilic catalysis'. Identify the missing intermediate/products **A**, **B**, **C** and **D**.



Q



(4 marks)

- 3.6 In the above reaction (3.5) pyridine acts as a catalyst because it is

(mark **X** in the correct box)

- i) more nucleophilic than benzene and is a poor leaving group.
- ii) less nucleophilic than benzene and is a poor leaving group.
- iii) less nucleophilic than benzene and is a good leaving group.
- iv) more nucleophilic than benzene and is a good leaving group.

(0.5 mark)

Problem 4

15 Marks

Reaction stoichiometry, kinetics and thermodynamics

Nitrosyl chloride (NOCl), is a yellow gas that is most commonly encountered as a decomposition product of *aqua regia*. It is toxic and irritating to the lungs. On heating NOCl decomposes as $2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$.

The enthalpy change (ΔH) for the formation of 1 mole of Cl_2 by the decomposition of NOCl is 75.3 kJ between 100 K to 600 K. The standard entropies ($S_{298\text{K}}^0$) of different species are as given below:

| Substance | NOCl | NO | Cl_2 |
|-----------------|------|-----|---------------|
| S_{298}^0 J/K | 264 | 211 | 223 |

- 4.1 Calculate K_p of the above decomposition reaction at 298 K. **(2 marks)**
- 4.2 Calculate the temperature at which K_p will be double the value at 298 K. **(1 mark)**
- 4.3 Calculate the temperature above which the reaction will become spontaneous. **(1 mark)**
- 4.4 A gaseous mixture of NO, Cl_2 and NOCl with partial pressures (in bar) 1.5, 0.88 and 0.065 respectively was taken at 475 K. Deduce whether the net reaction will lead to increase in NOCl concentration. **(2.5 marks)**
- 4.5 The initial rates of the reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ at different initial concentrations of the reactants are given below.

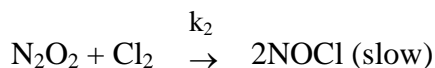
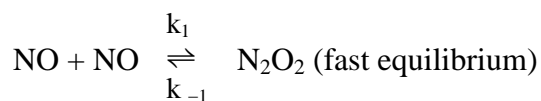
| [NO(g)] (mol dm ⁻³) | [Cl ₂ (g)] (mol dm ⁻³) | Initial Rate (mol dm ⁻³ s ⁻¹) |
|---------------------------------|---|--|
| 0.250 | 0.250 | 1.43 x 10 ⁻⁶ |
| 0.250 | 0.500 | 2.86 x 10 ⁻⁶ |
| 0.500 | 0.500 | 11.4 x 10 ⁻⁶ |

Write the kinetic rate law. **(1 mark)**

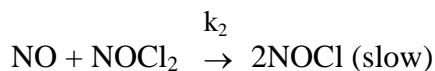
4.6 The rate constant for the formation of NOCl at 400 K is 2.0×10^4 times the value at 300 K. Calculate the activation energy for the reaction. **(1.5 marks)**

4.7 The following mechanisms (I and II) were proposed for the formation of NOCl.

Mechanism I



Mechanism II



Deduce which mechanism/s is/are consistent with the rate law arrived at in 4.5.

(3 marks)

4.8 The extent of a reaction is defined as $(n_i - n_i^0)/\nu_i$ where n_i^0 and n_i are the number of moles of reactant or product (species i) present respectively at the commencement of the reaction ($t = 0$) and at any time, t . ν_i is the stoichiometric coefficient of the substance "i" in the balanced equation. For the calculation of the extent of reaction, the stoichiometric coefficient is considered to be positive for products and negative for reactants. The extent of the reaction is the same for all reactants and products.

For the reaction, $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$, when 0.39 mol, 0.28 mol and 0.13 mol of NO, Cl_2 and NOCl respectively were taken initially, after certain time 0.18 mol of Cl_2 was found to remain in the reaction mixture. Calculate the extent of reaction with respect to NO and NOCl. **(1.5 marks)**

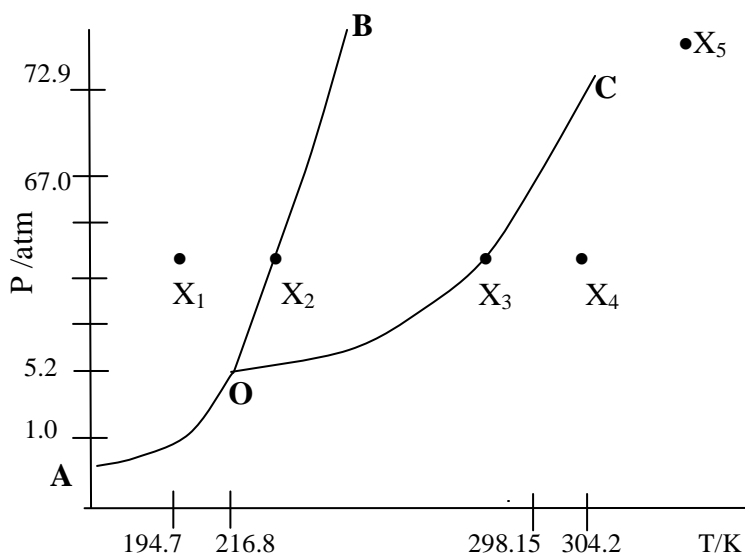
4.9 When reactants are not taken in stoichiometric proportions, a reaction will go to completion when one of the reactants is completely consumed. This reagent is known as the limiting reagent which will have the lowest value for $n_i^0 / |\nu_i|$. What is the limiting reagent in (4.8)? Calculate the extent of the reaction in (4.8), with respect to NOCl, when the reaction goes to completion. **(1.5 marks)**

Problem 5

14 Marks

Phase equilibrium

Phase diagram of a one-component system (S), is shown below. Answer the following questions with the help of this diagram.



5.1 What kind of phase change will take place if solid S is kept in the open under normal condition? (Mark X in the correct box)

- | | | | |
|----------------|--------------------------|--------------|--------------------------|
| a) Sublimation | <input type="checkbox"/> | b) Melting | <input type="checkbox"/> |
| c) Evaporation | <input type="checkbox"/> | d) No change | <input type="checkbox"/> |
- (1 mark)

5.2 Under which condition, are all the three phases of the system S in equilibrium?

(Mark X in the correct box).

- | | |
|--|--------------------------|
| a) $T > 304.2$ K and $P > 72.9$ atmosphere | <input type="checkbox"/> |
| b) $T = 216.8$ K and $P = 5.2$ atmosphere | <input type="checkbox"/> |
| c) $T > 304.2$ K | <input type="checkbox"/> |
| d) $P > 72.9$ atmosphere | <input type="checkbox"/> |
- (1mark)

5.3 Temperature of the system at X_1 is increased at constant pressure to reach X_4 . What are the phase/s of the system at the four different states X_1 to X_4 ? (2 marks)

5.4 Show graphically the heating curve (Temperature vs. Time) for the process in the above problem (5.3) with appropriate labeling of physical states. (2 marks)

5.5 If pressure is increased, the melting temperature of solid S will

(Mark X in the correct box)

a) Not change b) Increase

c) Decrease (1mark)

5.6 With the help of Clapeyron equation for phase change ($dP/dT = \Delta H^\circ / T\Delta V$), find what happens to the volume of the system at X₂ on heating? (1 mark)

5.7 What is the state of the system S, if it is heated in a sealed container above the critical temperature (304.2 K)? (1mark)

5.8 What happens to the system S at X₅, if pressure is changed slowly keeping temperature constant? (Mark X in the correct box)

a) At a higher pressure, the system will become liquid.

b) At a lower pressure, the system will become liquid.

c) The system will be in the same phase.

(1 mark)

Solutions

5.9 Raoult's law states that the partial pressure (p_1) of a solvent over a solution is given by the vapor pressure (p_1^0) of the pure solvent times the mole fraction (χ_1) of the solvent. Derive an expression relating lowering of vapor pressure with solute mole fraction. (1 mark)

5.10 The vapor pressure of water at 20°C is 17.54 mm of Hg and that of 10% (w/w) solution of an organic solute at the same temperature is 16.93 mm of Hg. Calculate the molecular weight of the solute using the expression derived in 5.9.

(1mark)

5.11 A solute is dissolved in two immiscible liquids in contact. Nernst's distribution law states that at equilibrium, the ratio of the concentration of the same molecular species

in the two phases is constant (K_D) at constant temperature.

Solute **A** is present as monomeric species **A** in solvent **S₁** and associates to form **A_n** in solvent **S₂**. Species **A** and **A_n** are in equilibrium with an equilibrium constant **K**.

a) What is the concentration of **A** in solvent **S₂**, if concentration of **A_n** is **C₂**?

(1 mark)

b) If the concentration of **A** in solvent **S₁** is **C₁**, calculate the distribution constant K_D of the solute.

(1mark)

Problem 6

13 Marks

Chemistry of Phosphorus and its compounds

Elemental phosphorus is recovered from the minerals fluorapatite and hydroxyapatite by carbon arc reduction. The resulting white phosphorus is a solid consisting of P_4 molecules.

6.1 Draw the geometrical and Lewis structures of P_4 . (1 mark)

6.2 White phosphorus reacts vigorously with aqueous sodium hydroxide resulting in the evolution of a gas and formation of sodium hypophosphite. Write the balanced equation for this reaction. (1 mark)

6.3 Sodium hypophosphite and sodium phosphite contain oxoanions of phosphorus.

a) Draw structures of these oxoanions.

b) State whether these oxoanions will act as an oxidizing agent or a reducing agent.

(Mark **X** in the correct box)

| | Oxidising agent | Reducing agent |
|---------------|-----------------|----------------|
| hypophosphite | | |
| phosphite | | |

c) Give appropriate reasons for your answers. (3 marks)

6.4 H_3PO_4 can be synthesized by the reaction of hydroxyapatite ($Ca_5(PO_4)_3F$) with H_2SO_4 . Write balanced equation for this reaction. (0.5 mark)

Complete combustion of phosphorus yields phosphorus(V) oxide P_4O_{10} , that has a cage structure.

- 6.5 Draw the structure of P_4O_{10} . (2 marks)
- 6.6 Calcium oxide reacts with P_4O_{10} to form calcium phosphate. Calculate the amount of CaO required (in grams) to react with 426 g of P_4O_{10} . (1 mark)
- Halides of phosphorus play an important role in the synthesis of a variety of phosphorus compounds.
- 6.7 Write balanced equation/s for the formation of triethyl phosphate from phosphorus trichloride. (1 mark)
- 6.8 Show the electronic configurations of P atom in i) ground and ii) excited states. State the hybridization of orbitals of P atom in PCl_3 and PCl_5 molecules. Predict the geometry of PCl_5 . (2.5 marks)
- 6.9 PCl_5 can react with NH_4Cl to form cyclophosphazines $(NPCl_2)_n$ where $n \geq 3$. Write the balanced equation for the formation of cyclophosphazine with $n = 3$ and draw the structure of this product. (1 mark)

Problem 7

11 Marks

Cobalt complexes

A pink solid compound (**A**) has the formula $CoCl_3 \cdot 5NH_3 \cdot H_2O$. An aqueous solution of this salt, which is also pink, on titration with $AgNO_3$ gives three moles of $AgCl$ per mole of **A**. Solid **A** on heating above $120^\circ C$ gives a purple solid (**B**) with the same ratio of $NH_3:Cl$. Compound **B** on titration with $AgNO_3$ gives two moles of $AgCl$ per mole of **B**.

- 7.1 Write the electronic configuration of cobalt in compound **A**. (0.5 mark)
- 7.2 Write the molecular formulae of **A** and **B** with their IUPAC names. (1.5 marks)

- 7.3 Valence bond theory is useful in predicting shapes of complexes. Show the arrangement of the electrons for cobalt in the low spin purple complex **B**. Predict the hybridization and the shape of this complex. (1.5 marks)

Although Valence bond theory is successful in predicting the shapes of complexes, it is unable to explain magnetic properties of coordination complexes. Crystal field theory (CFT) not only explains the magnetic properties but also accounts for color and spectra of these complexes. CFT is based on splitting of the **d** orbitals of the central metal in presence of ligands.

- 7.4 a) Using CFT draw the **d** orbital energy level diagram for the purple complex **B**. Label the energy levels and show the electron distribution. (1 mark)

b) Complex **B** is

paramagnetic

(Mark **X** in the correct box)

diamagnetic

(0.5 mark)

- 7.5 Using CFT, show the arrangement of the electrons on the central metal atom in the complex ion $[\text{Co}(\text{NH}_3)_6]^{2+}$. State with justification, whether $[\text{Co}(\text{NH}_3)_6]^{2+}$ is readily oxidized or not. (1.5 marks)

- 7.6 For the complex $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, draw the structures of possible stereoisomers and label them with stereochemical descriptors. (2 marks)

- 7.7 A set of equivalent protons in a molecule gives one signal in the ^1H NMR spectrum. The number of signal/s for the isomers drawn in 7.6 will be (1 mark)

- 7.8 Draw the structures of the following complexes and predict which one will be chiral.



where ox = oxalate ligand (represent the same as $\overset{\curvearrowright}{\text{O}}\text{O}$ in the answer).

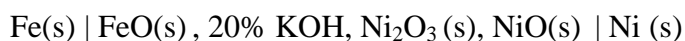
(1.5 marks)

Problem 8

10 Marks

Electrochemical cells

A secondary cell is one that can be recharged. Lead battery or the common car battery is an example of a secondary cell. Similarly, a battery using an alkali is known as the Edison cell. The Edison cell is represented as follows.



8.1 Write the half cell reactions and overall cell reaction for the above cell.

(1 mark)

8.2 If a student adds distilled water to the cell so that the concentration of KOH reduces to half of its original value, E_{cell} will (Mark **X** in the correct box)

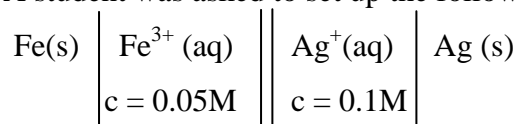
(i) get doubled

(ii) be halved

(iii) remain unchanged

(1 mark)

8.3 A student was asked to set up the following cell.



Calculate E^0 for this cell using the following data;

$$E^0_{\text{Fe}^{3+} \text{ (aq)}, \text{Fe}^{2+} \text{ (aq)}} = 0.771 \text{ V}; E^0_{\text{Fe}^{2+} \text{ (aq)} / \text{Fe(s)}} = -0.440 \text{ V}; E^0_{\text{Ag}^+ \text{ (aq)} / \text{Ag(s)}} = 0.799 \text{ V}$$

Hence calculate E_{cell} at 298 K.

(4 marks)

8.4 In a hurry, the student interchanged the electrodes, i.e. he placed the silver electrode in the solution of ferric ions (left hand half cell) and iron electrode in the solution of silver ions (right hand half cell). Write the reactions that may occur in each of the half cells due to this interchange.

(1 mark)

8.5 Assuming that the reaction in the left hand half cell in **8.4** reaches equilibrium, calculate

(i) equilibrium constant for the reaction.

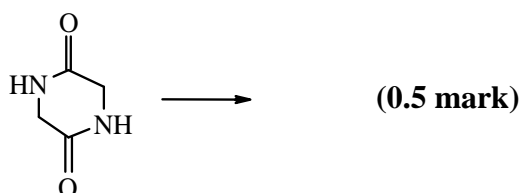
(ii) concentration of all the ions in the left hand half cell.

(3 marks)

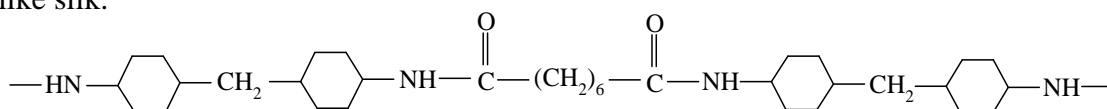
Problem 9
10 Marks
Polyamides

Several synthetic and naturally occurring polymers have amide linkage. Proteins which serve many functions in the biological systems are naturally occurring polyamides, made up of several amino acid residues.

9.1 Identify the product/s of complete hydrolysis of the compound shown below.



9.2 'Quina' which has the following structure is a synthetic polymer that feels very much like silk.



i) Is Quina a nylon or a polyester?

(0.5 mark)

ii) Identify the monomers used to synthesize Quina.

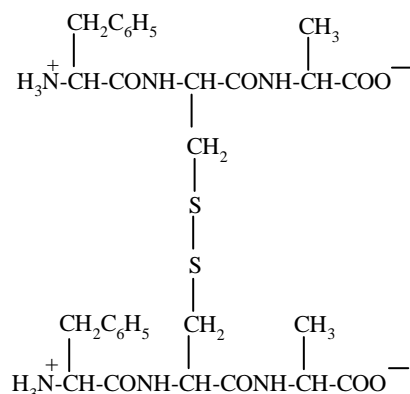
(1 mark)

9.3 Classify the following peptides as acidic, basic or neutral and state whether the charge on the peptide will be positive, negative or zero at pH = 6.0 (Refer to the table provided on page no.39).

| Peptide | Nature | | | Charge | | |
|---------------------|--------|-------|---------|----------|----------|------|
| | Acidic | Basic | Neutral | Positive | Negative | Zero |
| Gly-Leu-Val | | | | | | |
| Leu-Trp-Lys-Gly-Lys | | | | | | |
| Arg-Ser-Val | | | | | | |

(3 marks)

9.4 a) For the following peptide give the products of complete hydrolysis



(1.5 marks)

b) One of the above hydrolysis products is reduced in liver. Write the reaction showing the reduction. (1 mark)

9.5 The artificial sweetener *aspartame* is a methyl ester of synthetic dipeptide Asp-Phe

i) How many stereoisomers of *aspartame* are possible?

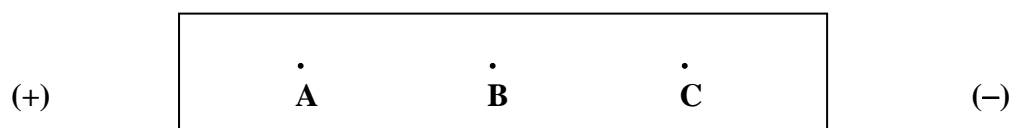
(0.5 mark)

ii) Draw the structure of *aspartame*.

(1 mark)

Electrophoresis is a method for separation of a mixture of amino acids. In this method, a sample of an amino acid mixture is placed at the centre of a piece of filter paper or a gel. The paper or the gel is then placed in a buffered solution between two electrodes and an electric field is applied. Depending on the net charge, an amino acid will move either to the anode or to the cathode.

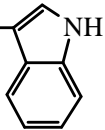
9.6 A mixture of arginine (pI=10.76), alanine (pI=6.02) and aspartic acid (pI=2.98) is separated by electrophoresis at pH = 5 (pI is the isoelectric point). Identify the amino acids **A**, **B** and **C** in the chromatogram given below.



(1 mark)

Table 1. Structure and pK_a values of a few α-amino acids

| α-Amino acid | Structure | pK _a value | | |
|---------------------|--|-----------------------|--------------------|------------|
| | | α-amino group | α-carboxylic group | Side chain |
| Alanine (Ala) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{array}$ | 9.7 | 2.3 | - |
| Arginine (Arg) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{NHCNH}_2 \end{array}$ | 9.0 | 2.2 | 12.5 |
| Aspartic acid (Asp) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{COOH} \end{array}$ | 9.8 | 2.1 | 3.9 |
| Cystine (Cys) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{SH} \end{array}$ | 10.8 | 1.8 | 8.3 |
| Glutamic acid (Glu) | $\begin{array}{c} \text{COOH} \\ \\ \text{H}_2\text{N}-\text{C}-\text{CH}_2-\text{CH}_2-\text{COH} \\ \qquad \qquad \qquad \\ \text{H} \qquad \qquad \qquad \text{O} \end{array}$ | 9.7 | 2.2 | 4.2 |
| Glycine (Gly) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ | 9.6 | 2.3 | - |
| Histidine (His) | $\begin{array}{c} \text{H} \\ \\ \text{CO}_2\text{H}-\text{C}-\text{CH}_2-\text{CH}_2-\text{N} \\ \qquad \qquad \qquad \diagup \quad \diagdown \\ \text{H}_2\text{N} \qquad \qquad \qquad \text{H} \quad \text{N} \end{array}$ | 9.2 | 1.8 | 6.0 |
| Leucine (Leu) | $\begin{array}{c} \text{COOH} \\ \\ \text{H}_2\text{N}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \qquad \qquad \qquad \\ \text{CH}_3 \end{array}$ | 9.6 | 2.4 | - |
| Lysine (Lys) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$ | 9.0 | 2.2 | 10.0 |
| Phenylalanine (Phe) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N}-\text{C}-\text{H} \\ \\ \text{CH}_2-\text{C}_6\text{H}_5 \end{array}$ | 9.1 | 1.8 | - |

| | | | | |
|---------------------|---|-----|-----|---|
| Serine (Ser) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N} - \text{C} - \text{H} \\ \\ \text{CH}_2\text{OH} \end{array}$ | 9.2 | 2.2 | - |
| Tryptophan (Trp) | $\begin{array}{c} \text{H} \\ \\ \text{CO}_2\text{H} - \text{C} - \text{CH}_2 - \text{Indole} \\ \\ \text{H}_2\text{N} \end{array}$  | 9.4 | 2.4 | - |
| Valine (Val) | $\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}_2\text{N} - \text{C} - \text{H} \\ \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ | 9.6 | 2.3 | - |