RAFFLES INSTITUTION
2019 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

26 September 2019
2 hours

Candidates answer on separate writing paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer all questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together, with the cover page on top. The cover page is found on page 2.

The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **16** printed pages.

RAFFLES INSTITUTION
2019 Year 6 Preliminary Examination
H2 Chemistry Paper 3

COVER SHEET

Name: ( )	**Class:**

For Examiner's Use Only

	Question	Marks
Section A	**1**	**/ 20**
	2	**/ 20**
	3	**/ 20**
Section B (Circle the question you have answered)	**4**	**/ 20**
	5	**/ 20**
Total		**/ 80**

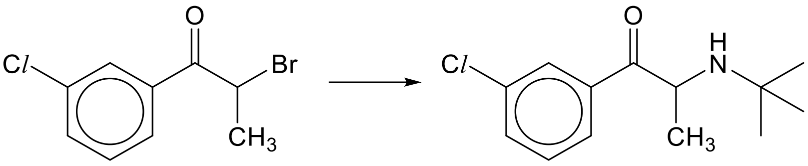
Attach this cover sheet to your writing paper.

Section A

Answer **all** the questions in this section.

1 Aminoketones are often used in the synthesis of drugs.

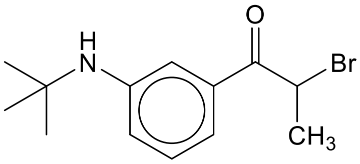
(a) The antidepressant, bupropion, is a drug which contains an aminoketone. The final step in the synthesis of bupropion involves the reaction between compound **G** and an amine.



compound **G** bupropion

(i) Write an equation for the reaction to form bupropion from compound **G**, showing clearly the structure of the amine used in the reaction. [1]

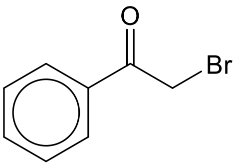
(ii) Explain why compound **H** was not formed in the reaction. [3]



compound **H**

(iii) Describe a simple chemical test to distinguish between compound **H** and bupropion. [2]

A different aminoketone is prepared by the reaction between 2-bromo-1-phenylethanone and triethylamine.



2-bromo-1-phenylethanone
$PhCOCH_2Br$

The rate of the reaction between $PhCOCH_2Br$ and triethylamine was investigated by the following method. This is Experiment 1.

Equal volumes of 0.10 mol dm^{-3} $PhCOCH_2Br$ and 0.10 mol dm^{-3} triethylamine were placed in a water bath at 30 °C. Both solutions were prepared in an organic solvent. After thermal equilibrium, the two solutions were mixed and kept at constant temperature throughout the reaction.

After one minute, a 5.0 cm^3 aliquot of the reaction mixture was collected and added to 10.0 cm^3 of sulfuric acid. The resulting mixture was analysed by titration. The procedure was repeated at different time intervals.

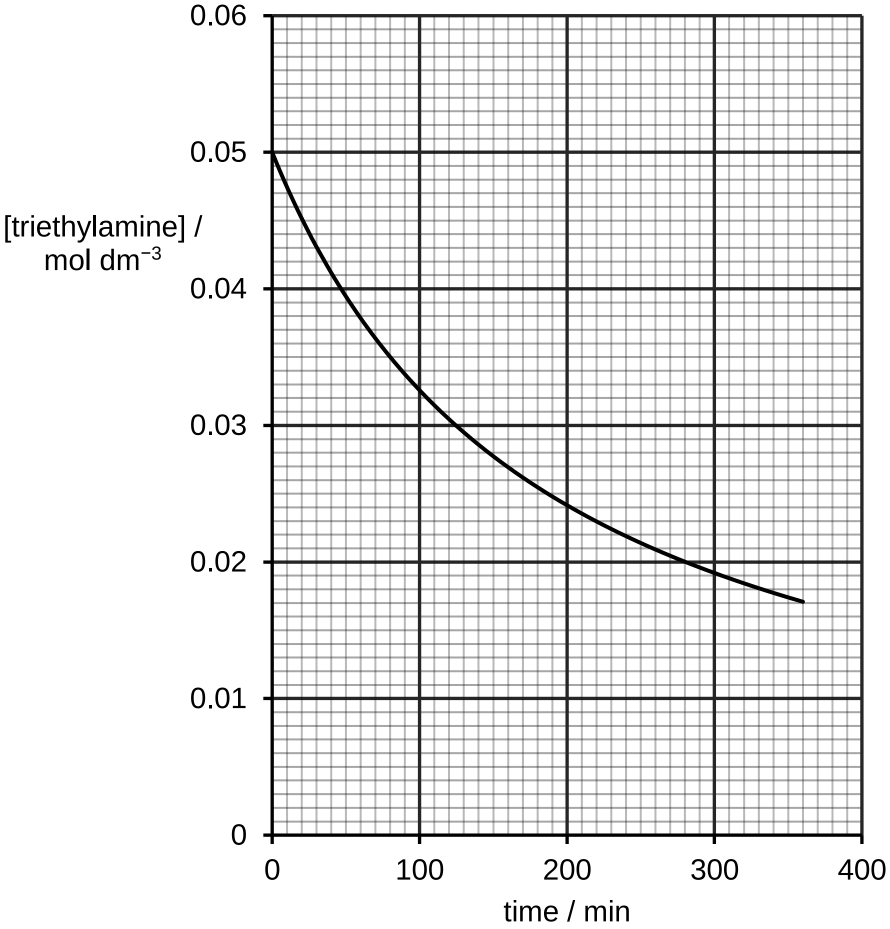
(b) **(i)** Why was the aliquot added to sulfuric acid? [1]

(ii) Why was it necessary for the $PhCOCH_2Br$ and triethylamine solutions to be kept at the same temperature before the start of the reaction? [1]

(iii) Explain, with the aid of a diagram, how changing the temperature of the reaction to 60 °C would affect the rate of the reaction. [2]

(c) A graph of the results of Experiment 1 is given in Figure 1.1.

Figure 1.1



Determine the initial rate of the reaction. [1]

(d) Further experiments were carried out using the same method with varying concentrations of the reagents at 30 °C.

Experiment	[$PhCOCH_2Br$] / mol dm^{-3}	[triethylamine] / mol dm^{-3}	relative initial rate
1	0.10	0.10	1
2	0.10	0.05	0.5
3	0.05	0.05	0.25

Deduce the rate equation for the reaction and state the units of the rate constant. [2]

(e) Based on your rate equation, name and draw the mechanism for the reaction between 2-bromo-1-phenylethanone and triethylamine. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

Represent 2-bromo-1-phenylethanone as $PhCOCH_2Br$ and triethylamine as R_3N. [3]

(f) Experiment 1 was modified by replacing $PhCOCH_2Br$ with other reagents. The reactions proceed via the same mechanism as in part **(e).**

In each case, state whether the initial rate of the reaction is higher or lower compared to Experiment 1. Give reasons for your answer.

(i) 0.10 mol dm^{-3} of $PhCOCH_2I$. [1]

(ii) 0.10 mol dm^{-3} of compound **G**. [1]

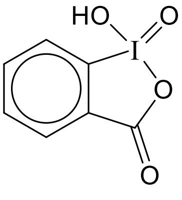
(iii) 0.10 mol dm^{-3} of (2-bromoethyl)benzene. [2]

[Total: 20]

2 There is a growing interest in using iodine and its compounds in research due to their unique and interesting physical and chemical properties.

(a) Iodine is the first element of group 17 that exists as a solid at room temperature. Explain why. [2]

2-Iodoxybenzoic acid (IBX) is used in organic syntheses to carry out unconventional reactions. The structure of IBX is shown below.

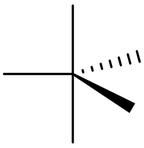


IBX

(b) IBX is an example of a chemical species which exhibits *hypervalency* – the ability of an atom in a molecule to hold more than 8 electrons in its valence shell.

(i) Identify the group 17 element(s) which is/are unable to exhibit hypervalency and explain why the element(s) is/are unable to do so. [2]

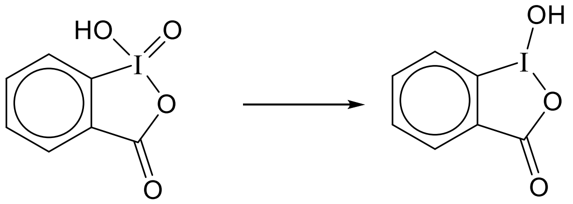
(ii) The iodine atom in IBX is surrounded by five regions of electron density arranged in a trigonal bipyramidal shape. A trigonal bipyramidal arrangement is shown below.



Draw a clear diagram of IBX with an arrangement of atoms around iodine, including lone pairs of electrons if any, which would result in the most stable structure. Briefly explain why the chosen arrangement is the most stable.

[2]

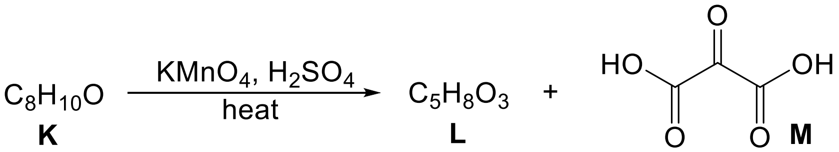
(c) A common use of IBX is to oxidise primary alcohols to aldehydes and secondary alcohols to ketones. In the process, IBX is converted to iodosobenzoic acid (IBA).



IBX IBA

(i) State the change in the oxidation state of iodine when IBX is converted to IBA. [1]

(ii) Alcohol **J** ($C_8H_{16}O$) is optically active and is one of four stereoisomers. When an excess of IBX was added to **J**, **K** ($C_8H_{10}O$) was obtained unexpectedly as the product. Further reactions were carried out to determine the structure of **K**.



Both compounds **K** and **L**

- are not optically active.
- give orange precipitates with 2,4-dinitrophenylhydrazine, but do not give a silver mirror with Tollens' reagent.

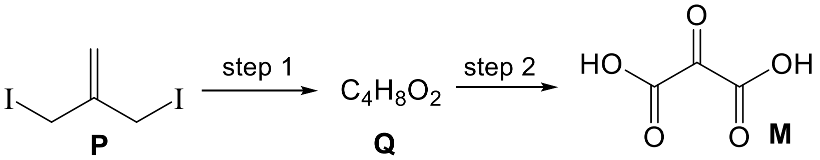
Compound **L** gives a yellow precipitate when heated with aqueous alkaline iodine, and produces effervescence with aqueous sodium carbonate.

Using the information above, you should

- deduce, with reasoning, the structures of **K** and **L**;
- draw the structure of a possible stereoisomer of **J**.

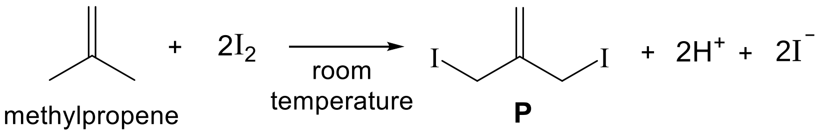
[7]

(d) Compound **M** can be made from compound **P** by a two-step synthesis.



Suggest reagents and conditions for steps 1 and 2, and draw the structure for compound **Q**. [3]

(e) Compound **P** can be prepared from the reaction of methylpropene with iodine.



It was found that the iodide ions act as an inhibitor for the reaction i.e. the presence of iodide slows down the rate of reaction.

(i) Suggest what can be deduced about the order of reaction with respect to iodide.
[1]

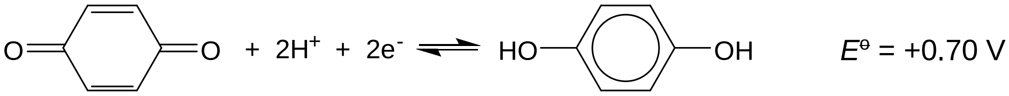
(ii) Researchers found it necessary to constantly remove the iodide by oxidising it to iodine at the anode of an electrolytic setup placed within the reaction mixture.

In an experiment, 0.10 mol of methylpropene was reacted with iodine. The electrolytic setup provided a current of 0.5 A.

Calculate the minimum time, in seconds, which the electrolytic setup should be kept running to remove all the iodide ions produced. [2]

[Total: 20]

3 **(a)** Halogens have different oxidising powers. Some halogens are capable of oxidising quinol to 1,4-benzoquinone.

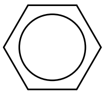
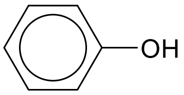
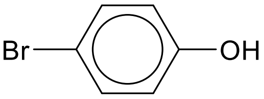
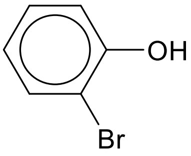
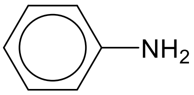
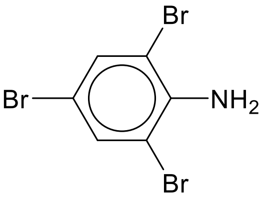


1, 4-benzoquinone quinol

With reference to the *Data Booklet*, choose one halogen which is capable of oxidising quinol to 1,4-benzoquinone and one halogen which does not oxidise quinol. Briefly explain your answers. [2]

(b) State the conditions required for Br_2 to react with ethene and with benzene. Account for the difference in the reaction conditions. [3]

(c) Benzene, phenol and phenylamine exhibit different reactivities towards reactions by electrophiles. An example used to illustrate their different reactivities is shown below.

reactions with Br_2 in CCl_4 at 5 °C	
compound	products formed
	no reaction
	 and 
	

(i) Explain what is meant by the term *electrophile*. [1]

(ii) Arrange the compounds, benzene, phenol and phenylamine, in increasing order of reactivity towards electrophilic substitution.

Explain your answer by considering any electronic effects exerted by the substituents. [3]

(iii) Compound **U**, C_6H_7NO, is amphoteric and forms a violet solution with neutral $FeCl_3$. On reacting with $COCl_2$, it forms **V**, $C_7H_5NO_2$.

Compound **U** also reacts with Br_2 in CCl_4 at 5 °C to form **W**.

Suggest structures for compounds **U**, **V** and **W**. [3]

(d) Phenol reacts with aqueous Br_2. In aqueous solution, phenol partially ionises to form phenoxide ion.

The mechanism for the reaction between phenoxide ion and aqueous Br_2 can be described as follows.

Step 1: A lone pair of electrons on the oxygen atom of H_2O is donated to a bromine atom in Br_2 to form a protonated hypobromous acid, H_2OBr^+.

Step 2: The phenoxide ion reacts with H_2OBr^+ to form an overall uncharged intermediate in a slow step. A H_2O molecule is lost in this step.

Step 3: The intermediate loses a proton from the carbon atom that is bonded to the bromine in a fast step.

Step 4: The mono-brominated phenoxide ion is protonated to form a mono-brominated phenol.

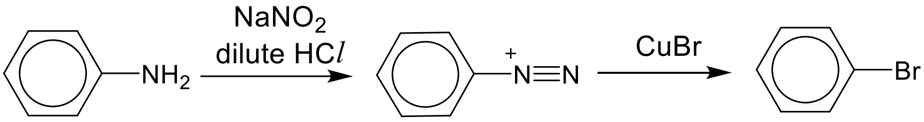
The mechanism continues until the final poly-substituted product is obtained.

(i) Write an equation for the reaction between phenol and aqueous Br_2. [1]

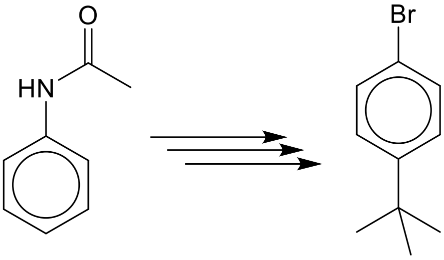
(ii) Draw the 4-step mechanism described above to show how phenol reacts with aqueous Br_2 to form 4-bromophenol. Show the following

- all charges and relevant lone pairs;
- displayed formulae of all compounds; and
- the movement of electron pairs by using curly arrows. [3]

(e) In the Sandmeyer reaction, phenylamine reacts with $NaNO_2$ and dilute HC*l* to form a diazonium salt which readily undergoes substitution reactions to produce new functional groups.



The following synthesis involves reactions in the order alkylation, hydrolysis and the Sandmeyer reaction.



(i) State the reagents and conditions, and draw the structures of the intermediate compounds of the synthesis. [3]

(ii) Suggest why the alkylation step must be carried out before hydrolysis to maximise the yield of the synthesis. [1]

[Total: 20]

Section B

Answer **one** question from this section.

4 Nickel naturally exists in the form of silicates, carbonates and oxides. These can be found as mineral ores in the crust of the Earth. One such mineral is gaspéite, which contains mainly nickel(II) carbonate. Some common impurities in gaspéite include oxides and carbonates of zinc and magnesium.

(a) With the use of the *Data Booklet*, explain the relative thermal stability of nickel(II) carbonate and magnesium carbonate. [2]

(b) To extract the nickel from gaspéite, the mineral is first heated strongly to convert the metal carbonates to metal oxides. The enthalpy change for the thermal decomposition of metal carbonates can be estimated using the lattice energies of the ionic solids.

The following data will be useful.

$CO_2(g) + O^{2-}(g) \rightarrow CO_3^{2-}(g)$	–1148 kJ mol^{-1}
lattice energy of NiO(s)	−3870 kJ mol^{-1}
lattice energy of $NiCO_3(s)$	–2980 kJ mol^{-1}

(i) Define *lattice energy*. [1]

(ii) Explain why the lattice energy of NiO is more negative than that of $NiCO_3$. [1]

(iii) Construct a fully labelled energy cycle to calculate the standard enthalpy change of thermal decomposition of nickel(II) carbonate. [3]

(c) Pure nickel metal can be obtained from its ore via the Mond process which has 3 steps.

Step 1:
Nickel(II) oxide in the ore reacts with hydrogen gas to give nickel and other impurities.

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

Step 2:
The impure nickel then reacts with carbon monoxide to form gaseous nickel carbonyl.

$$Ni(s) + 4CO(g) \rightarrow Ni(CO)_4(g)$$

Step 3:
The nickel carbonyl then undergoes decomposition to obtain the pure nickel metal.

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$$

The following data will be useful.

	$\Delta H_f^\ominus$ / kJ mol^{-1}
CO(g)	–110
$Ni(CO)_4(g)$	–603

(i) Using the data provided, calculate the $\Delta H^\ominus$ for step 2 of the Mond process. [1]

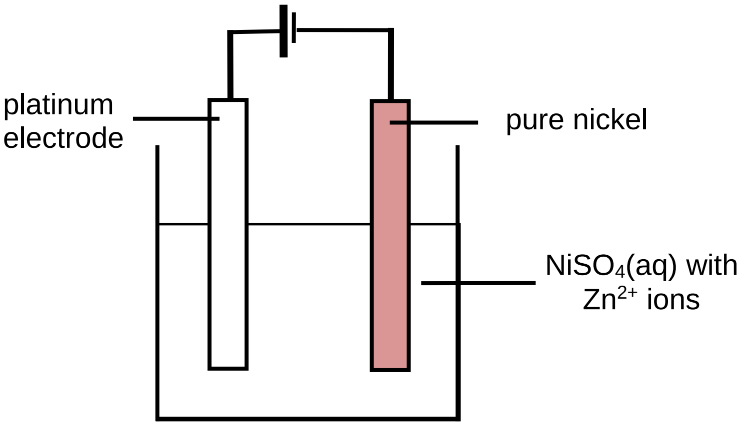
(ii) $\Delta S^\ominus$ for step 2 is −411 J mol^{-1} K^{-1}.

Explain the sign of $\Delta S^\ominus$ and calculate $\Delta G^\ominus$ for step 2. [2]

(iii) By considering the information above, explain, in terms of $\Delta G^\ominus$, why a high temperature is required for Step 3 of the Mond process. [2]

(iv) Using your answer to **(c)(i)** and given the enthalpy change of atomisation of Ni(s) is +430 kJ mol^{-1}, calculate the average bond energy of Ni–C in $Ni(CO)_4$(g). [2]

(d) Nickel can also be purified using an electrolytic cell. An ore containing nickel(II) oxide is reacted with sulfuric acid to obtain nickel(II) sulfate solution. Impurities including Zn^{2+} ions were also present. The solution was then neutralised before being used as the electrolyte of the cell. The setup of the cell is shown below.



(i) With reference to relevant $E^\ominus$ values, describe and explain the observations at both electrodes during electrolysis. [3]

Slight effervescence can be observed at the pure nickel electrode at the beginning of the electrolysis. The gas evolved extinguished a lighted splint with a ‘pop’ sound.

In addition, a small amount of green precipitate was formed near the nickel electrode.

(ii) Suggest the identity of the green precipitate and explain how it was formed. [2]

(iii) After running the electrolytic cell for some time, the pH of the electrolyte decreased and the green precipitate formed earlier dissolved.

Explain the above observations. [1]

[Total: 20]

5 The following equilibrium exists between nitrogen dioxide, NO_2, and its dimer, dinitrogen tetroxide, N_2O_4.

equilibrium 1 $2NO_2(g) \rightleftharpoons N_2O_4(g)$ $\Delta H < 0$
brown colourless

(a) **(i)** Draw the structure of NO_2, showing clearly all bonds and any non-bonding electrons.

State the shape of NO_2 and suggest a value for its bond angle. [3]

(ii) State and explain whether NO_2 is a polar or non-polar molecule. [1]

(iii) Use curly arrows to show how two molecules of NO_2 react to form one molecule of N_2O_4.

Hence, explain why the dimerisation of NO_2 is an exothermic reaction. [2]

(b) A gas syringe contains an equilibrium mixture of NO_2 and N_2O_4. The gas mixture is brown in colour.

The piston is pulled such that the volume of the gas mixture is increased suddenly. The mixture turns to a lighter brown immediately and then slowly darkens.

Explain the above observations. [2]

(c) In a series of experiments, an initial volume, V_i cm^3, of gaseous NO_2 was placed in a gas syringe and allowed to reach equilibrium under a constant, total pressure of *p* atm. The syringe was kept in a water bath maintained at *T* K. The total equilibrium volume was found to be V_{eqm} cm^3.

(i) Write the expression for the equilibrium constant, K_p, for equilibrium 1. [1]

(ii) The equilibrium volume of N_2O_4 in this system can be described by the following expression.

$$V_{\mathrm{N_2O_4}} = V_i - V_{eqm}$$

Use the above expression to derive the mole fraction of N_2O_4 at equilibrium, and hence, write the expression for the equilibrium partial pressure of N_2O_4. [1]

(iii) The equilibrium constant, K_p, can be described by the following equation.

$$K_p = \frac{(V_i - V_{eqm})V_{eqm}}{p(2V_{eqm} - V_i)^2}$$

In one experiment, 8.00 cm^3 of gaseous NO_2 established equilibrium under 1 atm in a water bath at 298.4 K. The total equilibrium volume was found to be 4.77 cm^3.

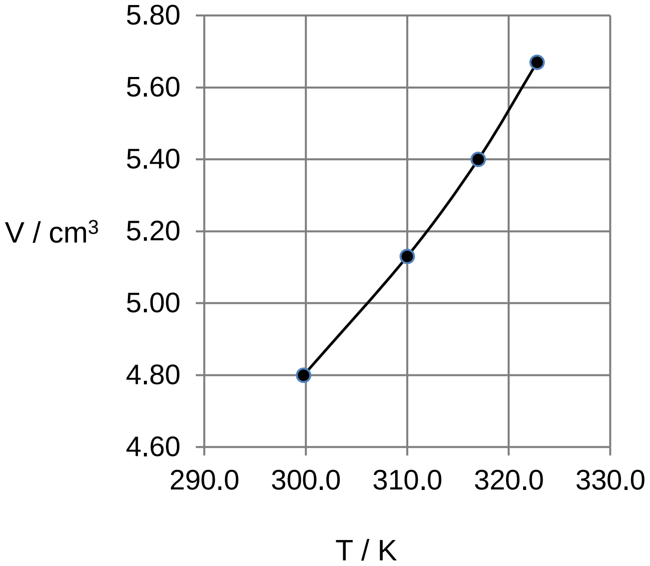
Calculate the value of K_p, in atm^{-1}, at T = 298.4 K. [1]

The experiment was repeated at different temperatures and some of the data obtained is shown in the table below.

temperature / K	value of K_p
299.8	6.00
310.0	2.88
317.0	1.79
322.8	1.18

(iv) By considering the data in the table, explain how the dimerisation of NO_2 can be deduced to be an exothermic reaction. [2]

(v) The experimental data was also used to plot a graph of total equilibrium volume against temperature. The graph is given below.



Suggest why the total equilibrium volume of the NO_2/N_2O_4 gas mixture increases with temperature, and at an increasing rate. [2]

(d) Helium is said to behave like an ideal gas.

(i) Explain why helium behaves like an ideal gas. [2]

X is an elemental, diatomic gas with strongly oxidising properties.

(ii) Given that **X** has a density of 3.2 kg m^{-3} at s.t.p., determine the identity of **X**. You may assume **X** behaves like an ideal gas at s.t.p. [2]

(iii) On the same axes, sketch graphs of pV/RT against p for 1 mol of He and 1 mol of **X**. [1]

[Total: 20]