HL Paper 2

Urea, $(H_2N)_2CO$, is excreted by mammals and can be used as a fertilizer.

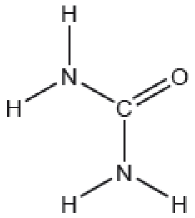
Urea can also be made by the direct combination of ammonia and carbon dioxide gases.

$$2NH_3(g) + CO_2(g) \rightleftharpoons (H_2N)_2CO(g) + H_2O(g) \quad \Delta H < 0$$

a.i. Calculate the percentage by mass of nitrogen in urea to two decimal places using section 6 of the data booklet. [2]

a.ii. Suggest how the percentage of nitrogen affects the cost of transport of fertilizers giving a reason. [1]

b. The structural formula of urea is shown. [3]



Predict the electron domain and molecular geometries at the nitrogen and carbon atoms, applying the VSEPR theory.

	Electron domain geometry	**Molecular geometry**
Nitrogen	. . . .	. . . .
Carbon	. . . .	trigonal planar

c. Urea can be made by reacting potassium cyanate, KNCO, with ammonium chloride, NH_4Cl. [2]

$$KNCO(aq) + NH_4Cl(aq) \rightarrow (H_2N)_2CO(aq) + KCl(aq)$$

Determine the maximum mass of urea that could be formed from 50.0 cm^3 of 0.100 mol dm^{-3} potassium cyanate solution.

d.i. State the equilibrium constant expression, K_c. [1]

d.ii. Predict, with a reason, the effect on the equilibrium constant, K_c, when the temperature is increased. [1]

d.iii. Determine an approximate order of magnitude for K_c, using sections 1 and 2 of the data booklet. Assume $\Delta G^\ominus$ for the forward reaction is approximately +50 kJ at 298 K. [2]

e.i. Suggest one reason why urea is a solid and ammonia a gas at room temperature. [1]

e.ii. Sketch two different hydrogen bonding interactions between ammonia and water. [2]

f. The combustion of urea produces water, carbon dioxide and nitrogen. [2]

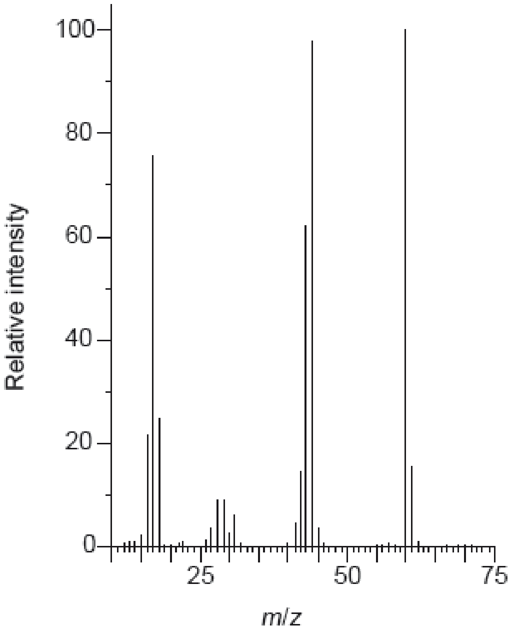
Formulate a balanced equation for the reaction.

g. Calculate the maximum volume of CO_2, in cm^3, produced at STP by the combustion of 0.600 g of urea, using sections 2 and 6 of the data booklet. [1]

h. Describe the bond formation when urea acts as a ligand in a transition metal complex ion. [2]

i. The C–N bonds in urea are shorter than might be expected for a single C–N bond. Suggest, in terms of electrons, how this could occur. [1]

j. The mass spectrum of urea is shown below. [2]



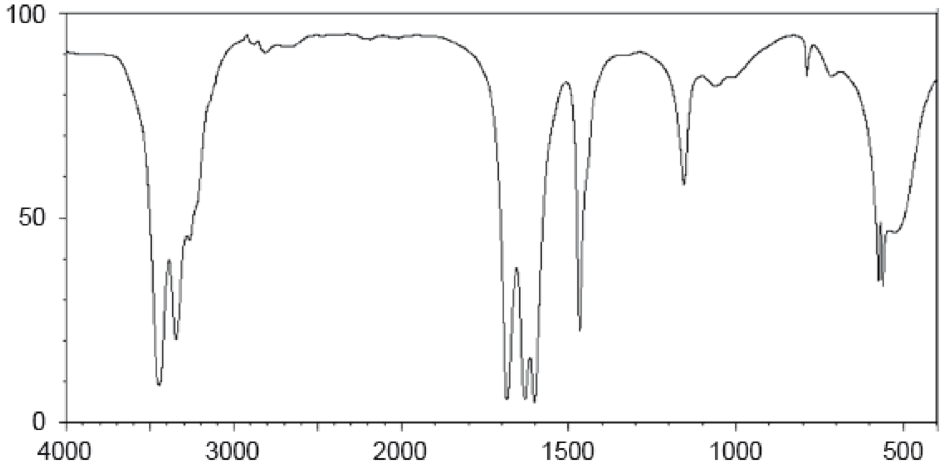
[Source: http://sdbs.db.aist.go.jp]

Identify the species responsible for the peaks at *m*/*z* = 60 and 44.

60:

44:

k. The IR spectrum of urea is shown below. [2]



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Identify the bonds causing the absorptions at 3450 cm^{-1} and 1700 cm^{-1} using section 26 of the data booklet.

3450 cm^{-1}:

. . . .

1700 cm^{-1}:

. . . .

l.i. Predict the number of signals in the ^{1}H NMR spectrum of urea. [1]

l.ii. Predict the splitting pattern of the ^{1}H NMR spectrum of urea. [1]

l.iii. Outline why TMS (tetramethylsilane) may be added to the sample to carry out ^{1}H NMR spectroscopy and why it is particularly suited to this role. [2]

But-2-ene belongs to the homologous series of the alkenes.

The time taken to produce a certain amount of product using different initial concentrations of C_4H_9Br and NaOH is measured. The results are shown in the following table.

Reaction	[C_4H_9Br] / 10^{-2} mol dm^{-3}	[NaOH] / 10^{-3} mol dm^{-3}	t / s
A	1.0	2.0	46
B	2.0	2.0	23
C	2.0	4.0	23

a.i. Outline **three** features of a homologous series. [3]

a.ii. Describe a test to distinguish but-2-ene from butane, including what is observed in **each** case. [2]

a.iii 2-bromobutane can be produced from but-2-ene. State the equation of this reaction using structural formulas. [1]

a.iv.State what is meant by the term *stereoisomers*. [1]

a.v.Explain the existence of geometrical isomerism in but-2-ene. [2]

c.i. Deduce the order of reaction with respect to C_4H_9Br and NaOH, using the data above. [3]

C_4H_9Br

NaOH:

c.ii.Deduce the rate expression. [1]

c.iii.Based on the rate expression obtained in (c) (ii) state the units of the rate constant, k. [1]

d.ii.Halogenalkanes can react with NaOH via S_N1 and S_N2 type mechanisms. Explain why C_4H_9Br reacts via the mechanism described in (d) (i). [1]

d.iii.Identify the rate-determining step of this mechanism. [1]

The percentage of iron(II) ions, Fe^{2+}, in a vitamin tablet can be estimated by dissolving the tablet in dilute sulfuric acid and titrating with standard potassium manganate(VII) solution, $KMnO_4(aq)$. During the process iron(II) is oxidized to iron(III) and the manganate(VII) ion is reduced to the manganese(II) ion, $Mn^{2+}(aq)$. It was found that one tablet with a mass of 1.43 g required $11.6\ cm^3$ of $2.00 \times 10^{-2}\ mol\,dm^{-3}\ KMnO_4(aq)$ to reach the end-point.

a.i. State the half-equation for the oxidation of the iron(II) ions. [1]

a.ii.State the half-equation for the reduction of the MnO_4^- ions in acidic solution. [1]

a.iii.Deduce the overall redox equation for the reaction. [1]

b.i.Calculate the amount, in moles, of MnO_4^- ions present in $11.6\ cm^3$ of $2.00 \times 10^{-2}\ mol\,dm^{-3}\ KMnO_4(aq)$. [1]

b.ii.Calculate the amount, in moles, of Fe^{2+} ions present in the vitamin tablet. [1]

b.iii.Determine the percentage by mass of Fe^{2+} ions present in the vitamin tablet. [2]

A voltaic cell was set up, using the standard hydrogen electrode as a reference electrode and a standard $Cu^{2+}(aq)/Cu(s)$ electrode.

Another voltaic cell was set up, using a $Sn^{2+}(aq)/Sn(s)$ half-cell and a $Cu^{2+}(aq)/Cu(s)$ half-cell under standard conditions.

Water in a beaker at a pressure of $1.01 \times 10^5 \text{ Pa}$ and a temperature of 298 K will not spontaneously decompose. However, decomposition of water can be induced by means of electrolysis.

a. Define *oxidation* in terms of oxidation number. [1]

b.i. Deduce the balanced chemical equation for the redox reaction of copper, Cu(s), with nitrate ions, $\text{NO}^{3-}(\text{aq})$, **in acid**, to produce copper(II) ions, $\text{Cu}^{2+}(\text{aq})$, and nitrogen(IV) oxide, $\text{NO}_2(\text{g})$. [2]

b.ii. Deduce the oxidizing and reducing agents in this reaction. [1]

Oxidizing agent:

Reducing agent:

c.i. Describe the standard hydrogen electrode including a fully labelled diagram. [3]

c.ii. Define the term *standard electrode potential*, E^{Θ}. [1]

c.iii. Deduce a balanced chemical equation, including state symbols, for the overall reaction which will occur spontaneously when the two half-cells are connected. [2]

d.i. Draw a fully labelled diagram of the voltaic cell, showing the positive electrode (cathode), the negative electrode (anode) and the direction of electron movement through the external circuit. [3]

d.ii. Using Table 14 of the Data Booklet, calculate the cell potential, E^{Θ}_{cell}, in V, when the two half-cells are connected. [1]

e.i. Deduce the sign of the standard free energy change, ΔG^{Θ}, for any non-spontaneous reaction. [1]

e.ii. State why dilute sulfuric acid needs to be added in order for the current to flow in the electrolytic cell. [1]

e.iii. State why copper electrodes cannot be used in the electrolysis of water. Suggest instead suitable **metallic** electrodes for this electrolysis process. [1]

e.iv. Deduce the half-equations for the reactions occurring at the positive electrode (anode) and the negative electrode (cathode). [2]

Positive electrode (anode):

Negative electrode (cathode):

e.v. Deduce the overall cell reaction, including state symbols. [1]

e.vi. Draw a fully labelled diagram of the electrolytic cell, showing the positive electrode (anode) and the negative electrode (cathode). [2]

e.vii. Comment on what is observed at both electrodes. [1]

f. Two electrolytic cells are connected in series (the same current passes through each cell). One cell for the electrolysis of water produces 100 cm^3 of oxygen, measured at 273 K and $1.01 \times 10^5\ \mathrm{Pa}$. The second cell contains molten lead(II) bromide, $\mathrm{PbBr_2}$. Determine the mass, in g, of lead produced. [2]

In December 2010, researchers in Sweden announced the synthesis of N,N–dinitronitramide, $\mathrm{N(NO_2)_3}$. They speculated that this compound, more commonly called trinitramide, may have significant potential as an environmentally friendly rocket fuel oxidant.

a. Methanol reacts with trinitramide to form nitrogen, carbon dioxide and water. Deduce the coefficients required to balance the equation for this reaction. [1]

$$\_\_\ \mathrm{N(NO_2)_3(g)} + \_\_\ \mathrm{CH_3OH(l)} \rightarrow \_\_\ \mathrm{N_2(g)} + \_\_\ \mathrm{CO_2(g)} + \_\_\ \mathrm{H_2O(l)}$$

c. Calculate the enthalpy change, in $\mathrm{kJ\,mol^{-1}}$, when one mole of trinitramide decomposes to its elements, using bond enthalpy data from Table 10 of the Data Booklet. Assume that all the N–O bonds in this molecule have a bond enthalpy of $305\ \mathrm{kJ\,mol^{-1}}$. [3]

d. The entropy change, ΔS, for the decomposition of trinitramide has been estimated as $+700\ \mathrm{J\,K^{-1}mol^{-1}}$. Comment on the sign of ΔS. [2]

e. Using $+700\ \mathrm{J\,K^{-1}mol^{-1}}$ as the value for the entropy change, along with your answer to part (c), calculate ΔG, in $\mathrm{kJ\,mol^{-1}}$, for this reaction at 300 K. (If you did not obtain an answer for part (c), then use the value $-1000\ \mathrm{kJ\,mol^{-1}}$, but this is not the correct value.) [3]

f. Explain how changing the temperature will affect whether or not the decomposition of trinitramide is spontaneous. [2]

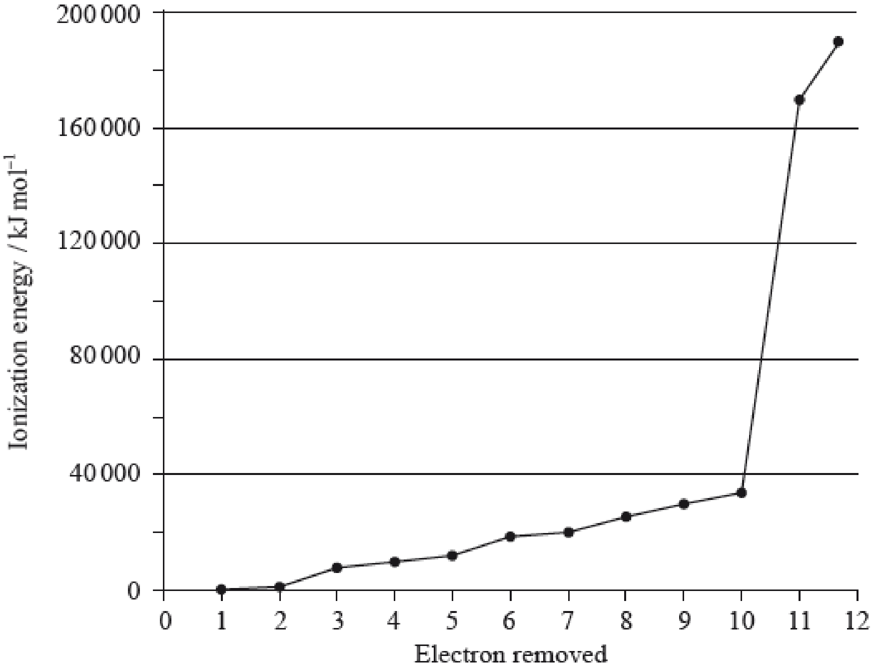
g. Outline how the length of the N–N bond in trinitramide compares with the N–N bond in nitrogen gas, $\mathrm{N_2}$. [2]

h. Deduce the N–N–N bond angle in trinitramide and explain your reasoning. [3]

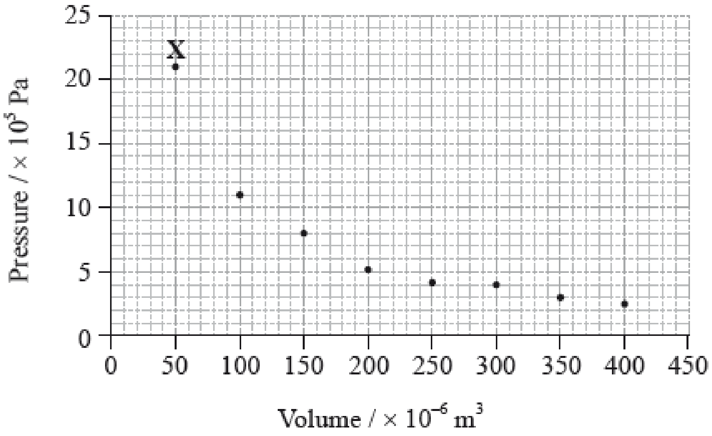
i. Predict, with an explanation, the polarity of the trinitramide molecule. [2]

A sample of magnesium contains three isotopes: magnesium-24, magnesium-25 and magnesium-26, with abundances of 77.44%, 10.00% and 12.56% respectively.

A graph of the successive ionization energies of magnesium is shown below.



The graph below shows pressure and volume data collected for a sample of carbon dioxide gas at 330 K.



a. (i) Calculate the relative atomic mass of this sample of magnesium correct to **two** decimal places. [4]

(ii) Predict the relative atomic radii of the three magnesium isotopes, giving your reasons.

b. (i) Explain the increase in ionization energy values from the 3rd to the 8th electrons. [3]

(ii) Explain the sharp increase in ionization energy values between the 10th and 11th electrons.

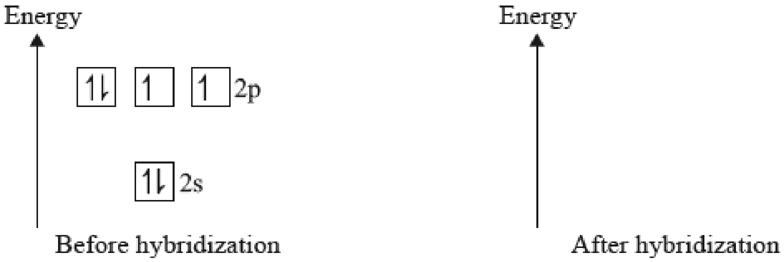
c. (i) Magnesium reacts with oxygen to form an ionic compound, magnesium oxide. Describe how the ions are formed, and the structure and bonding in magnesium oxide. [4]

(ii) Carbon reacts with oxygen to form a covalent compound, carbon dioxide. Describe what is meant by a covalent bond.

(iii) State why magnesium and oxygen form an ionic compound while carbon and oxygen form a covalent compound.

d. (i) Predict the type of hybridization of the carbon and oxygen atoms in $\mathrm{CO_2}$. [7]

(ii) Sketch the orbitals of an oxygen atom in $\mathrm{CO_2}$ on the energy level diagram provided, including the electrons that occupy each orbital.



(iii) Define the term electronegativity.

(iv) Explain why oxygen has a larger electronegativity than carbon.

e. (i) Draw a best-fit curve for the data on the graph. [4]

(ii) Use the data point labelled **X** to determine the amount, in mol, of carbon dioxide gas in the sample.

f. (i) Most indicators are weak acids. Describe qualitatively how indicators work. [3]

(ii) Identify a suitable indicator for a titration between a weak acid and a strong base, using Table 16 of the Data Booklet.

The electron configuration of chromium can be expressed as $\mathrm{[Ar]4s^x3d^y}$.

Hydrogen and nitrogen(II) oxide react according to the following equation.

$$\mathrm{2H_2(g) + 2NO(g) \rightleftharpoons N_2(g) + 2H_2O(g)}$$

At time = t seconds, the rate of the reaction is

$$\mathrm{rate} = k[\mathrm{H_2(g)}][\mathrm{NO(g)}]^2$$

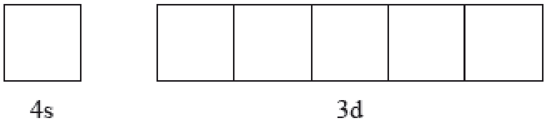
When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:

$$[\mathrm{Cu(H_2O)_6}]^{2+}(\mathrm{aq}) + 4\mathrm{Cl^-}(\mathrm{aq}) \rightarrow [\mathrm{CuCl_4}]^{2-}(\mathrm{aq}) + 6\mathrm{H_2O(l)}$$

a.i. Explain what the square brackets around argon, [Ar], represent. [1]

a.ii. State the values of x and y. [1]

a.iii. Annotate the diagram below showing the 4s and 3d orbitals for a chromium atom using an arrow, ↿ and ⇂, to represent a spinning electron. [1]



b.i. Explain precisely what the square brackets around nitrogen(II) oxide, [NO(g)], represent in this context. [1]

b.ii. Deduce the units for the rate constant k. [1]

c.i. Explain what the square brackets around the copper containing species represent. [1]

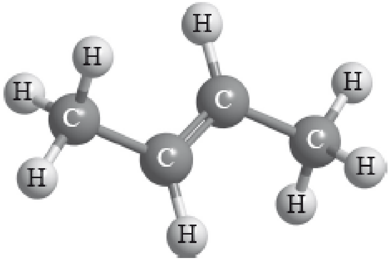
c.ii. Explain why the $[\mathrm{Cu(H_2O)_6}]^{2+}$ ion is coloured and why the $[\mathrm{CuCl_4}]^{2-}$ ion has a different colour. [2]

d. Some words used in chemistry can have a specific meaning which is different to their meaning in everyday English. [1]

State what the term *spontaneous* means when used in a chemistry context.

Geometrical isomerism and optical isomerism are two sub-groups of stereoisomerism in organic chemistry.

Compound **P** has the following three-dimensional structure. **P** also has geometrical isomers.

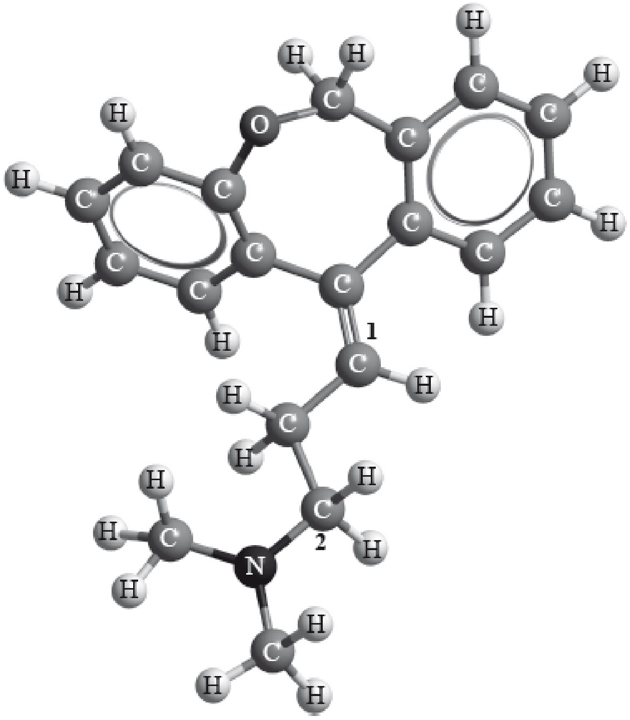


P

Menthol can be used in cough medicines. The compound contains C, H and O only.

a. Describe what is meant by the term *stereoisomers*. [1]

b. Geometrical isomers have different physical properties and many drugs, such as doxepin (which has antidepressant properties), have geometrical isomers. [1]



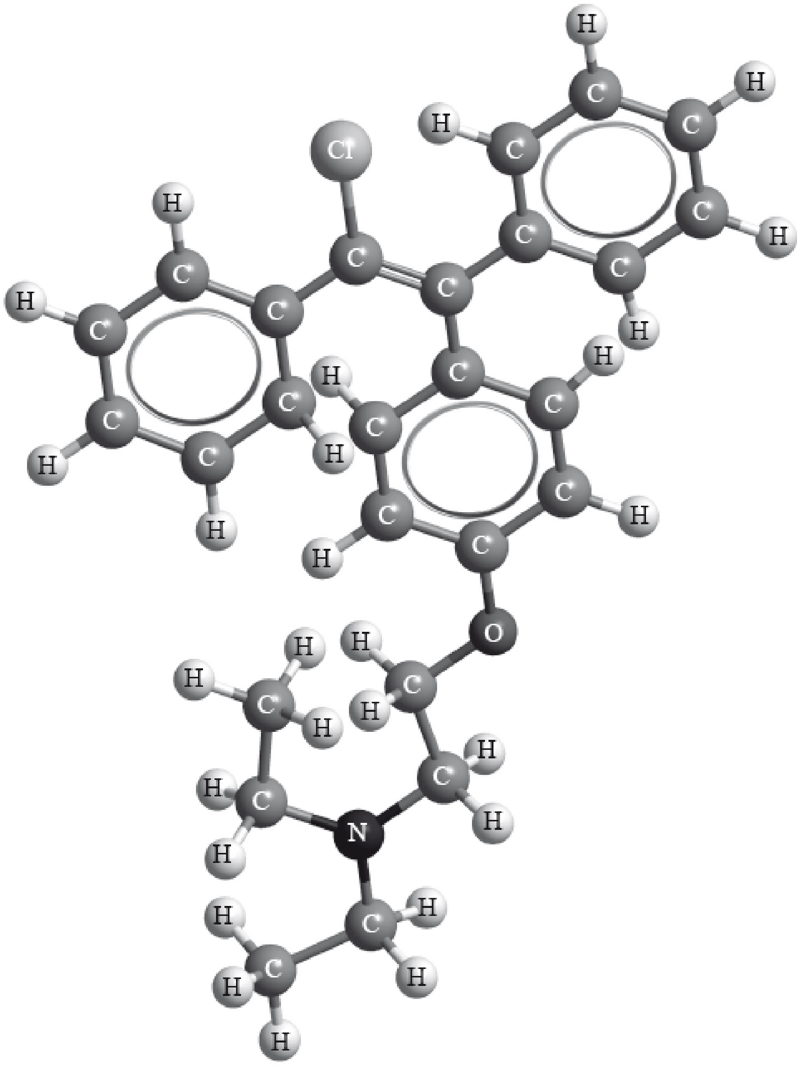
Example of a geometrical isomer of doxepin

For each of the carbon atoms labelled **1** and **2** in doxepin, deduce the type of hybridization involved (sp, sp^2 or sp^3).

1:

2:

c. Clomifene, a fertility drug, whose three-dimensional structure is represented below, also has geometrical isomers. [1]



Identify the name of **one** functional group present in clomifene.

d.i. Draw any **two** other isomers of **P**. [2]

d.ii. Apply IUPAC rules to state the names of all the straight-chain isomers of compounds of molecular formula C_4H_8 (including **P**). [2]

d.iii. State the structural formula of the organic products, **Q**, **R**, **S** and **T**, formed in the following reactions. [4]

$CH_3CH{=}CHCH_3 \quad + \quad HBr\,(g) \longrightarrow$ **Q**

Q:

$CH_3CH{=}CHCH_3 \xrightarrow[\text{(2) } H_2O(l)]{\text{(1) concentrated } H_2SO_4(aq)}$ **R**

R:

$CH_3CH{=}CHCH_3 \quad + \quad Br_2\,(aq) \longrightarrow$ **S**

S:

Q $\quad + \quad OH^-\,(aq) \longrightarrow$ **T**

T:

d.iv. Suggest **one** suitable mechanism for the reaction of **Q** with aqueous sodium hydroxide to form **T**, using curly arrows to represent the movement of electron pairs. [4]

d.v. State the structural formula of the organic product formed, **U**, when **R** is heated under reflux with acidified potassium dichromate(VI). [1]

d.vi. Apply IUPAC rules to state the name of this product, **U**. [1]

e.i. When a 6.234×10^{-2} g of the compound was combusted, 1.755×10^{-1} g of carbon dioxide and 7.187×10^{-2} g of water were produced. Determine the molecular formula of the compound showing your working, given that its molar mass is $M = 156.30\ \text{g mol}^{-1}$. [4]

e.ii. Menthol occurs naturally and has several isomers. State the structural feature of menthol which is responsible for it having enantiomers. [1]

e.iii. State the instrument used to distinguish between each of the two enantiomers, and how they could be distinguished using this instrument. [1]

e.iv. Compare the physical and chemical properties of enantiomers. [2]

Physical properties:

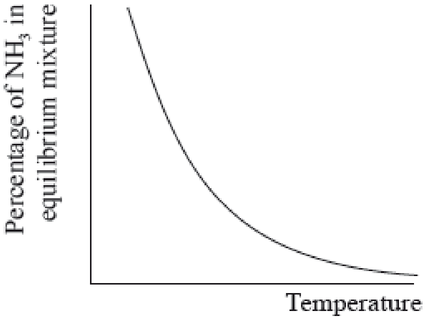
Chemical properties:

The Haber process enables the large-scale production of ammonia needed to make fertilizers.

The equation for the Haber process is given below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The percentage of ammonia in the equilibrium mixture varies with temperature.



Ammonia can be converted into nitric acid, $HNO_3(aq)$, and hydrocyanic acid, HCN(aq). The pK_a of hydrocyanic acid is 9.21.

A student decided to investigate the reactions of the two acids with separate samples of $0.20\ mol\,dm^{-3}$ sodium hydroxide solution.

a. (i) Use the graph to deduce whether the forward reaction is exothermic or endothermic and explain your choice. [9]

(ii) State and explain the effect of increasing the pressure on the yield of ammonia.

(iii) Deduce the equilibrium constant expression, K_c, for the reaction.

(iv) A mixture of 1.00 mol N_2 and 3.00 mol H_2 was placed in a $1.0\ dm^3$ flask at 400 °C. When the system was allowed to reach equilibrium, the concentration of was found to be $0.062\ mol\,dm^{-3}$. Determine the equilibrium constant, K_c, of the reaction at this temperature.

(v) Iron is used as a catalyst in the Haber process. State the effect of a catalyst on the value of K_c.

b. (i) Distinguish between the terms *strong* and *weak acid* and state the equations used to show the dissociation of each acid in aqueous solution. [9]

(ii) Deduce the expression for the ionization constant, K_a, of hydrocyanic acid and calculate its value from the pK_a value given.

(iii) Use your answer from part (b) (ii) to calculate the $[H^+]$ and the pH of an aqueous solution of hydrocyanic acid of concentration $0.108\ mol\,dm^{-3}$. State **one** assumption made in arriving at your answer.

c. A small piece of magnesium ribbon is added to solutions of nitric and hydrocyanic acid of the same concentration at the same temperature. [2]

Describe **two** observations that would allow you to distinguish between the two acids.

d. (i) Calculate the volume of the sodium hydroxide solution required to react exactly with a $15.0\ cm^3$ solution of $0.10\ mol\,dm^{-3}$ nitric acid. [3]

(ii) The following hypothesis was suggested by the student: "Since hydrocyanic acid is a weak acid it will react with a smaller volume of the $0.20\ mol\,dm^{-3}$ sodium hydroxide solution." Comment on whether or not this is a valid hypothesis.

(iii) Use Table 16 of the Data Booklet to identify a suitable indicator for the titration of sodium hydroxide and hydrocyanic acid.

The concentration of a solution of a weak acid, such as ethanedioic acid, can be determined

by titration with a standard solution of sodium hydroxide, NaOH (aq).

c. 5.00 g of an impure sample of hydrated ethanedioic acid, $(COOH)_2 \cdot 2H_2O$, was dissolved in water to make 1.00 dm^3 of solution. 25.0 cm^3 samples of this solution were titrated against a 0.100 mol dm^{-3} solution of sodium hydroxide using a suitable indicator. [6]

$$(COOH)_2\text{ (aq)} + 2NaOH\text{ (aq)} \rightarrow (COONa)_2\text{ (aq)} + 2H_2O\text{ (l)}$$

The mean value of the titre was 14.0 cm^3.

(i) Suggest a suitable indicator for this titration. Use section 22 of the data booklet.

(ii) Calculate the amount, in mol, of NaOH in 14.0 cm^3 of 0.100 mol dm^{-3} solution.

(iii) Calculate the amount, in mol, of ethanedioic acid in each 25.0 cm^3 sample.

(iv) Determine the percentage purity of the hydrated ethanedioic acid sample.

d. Draw the Lewis (electron dot) structure of the ethanedioate ion, $^{-}OOCCOO^{-}$. [1]

e. Outline why all the C–O bond lengths in the ethanedioate ion are the same length and suggest a value for them. Use section 10 of the data booklet. [2]

f. Explain how ethanedioate ions act as ligands. [2]

Alkenes, alcohols and esters are three families of organic compounds with many commercial uses.

An ester which gives apples their characteristic smell contains C, H and O. When 3.00×10^{-3} g of this ester were completely combusted, 6.93×10^{-3} g of CO_2 and 2.83×10^{-3} g of H_2O were produced.

a.i. State what is meant by the term *stereoisomers*. [1]

b.i. Determine the empirical formula of the ester, showing your working. [4]

b.ii. The molar mass of the ester is $116.18\ g\,mol^{-1}$. Determine its molecular formula. [1]

c.iii 2-bromobutane is optically active. Draw the two enantiomers of 2-bromobutane and compare their physical and chemical properties. [2]

Reaction kinetics can be investigated using the iodine clock reaction. The equations for two reactions that occur are given below.

Reaction A: $H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$

Reaction B: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Reaction B is much faster than reaction A, so the iodine, I_2, formed in reaction A immediately reacts with thiosulfate ions, $S_2O_3^{2-}$, in reaction B, before it can react with starch to form the familiar blue-black, starch-iodine complex.

In one experiment the reaction mixture contained:

5.0 ± 0.1 $\mathrm{cm^3}$ of 2.00 $\mathrm{mol\,dm^{-3}}$ hydrogen peroxide (H_2O_2)

5.0 ± 0.1 $\mathrm{cm^3}$ of 1% aqueous starch

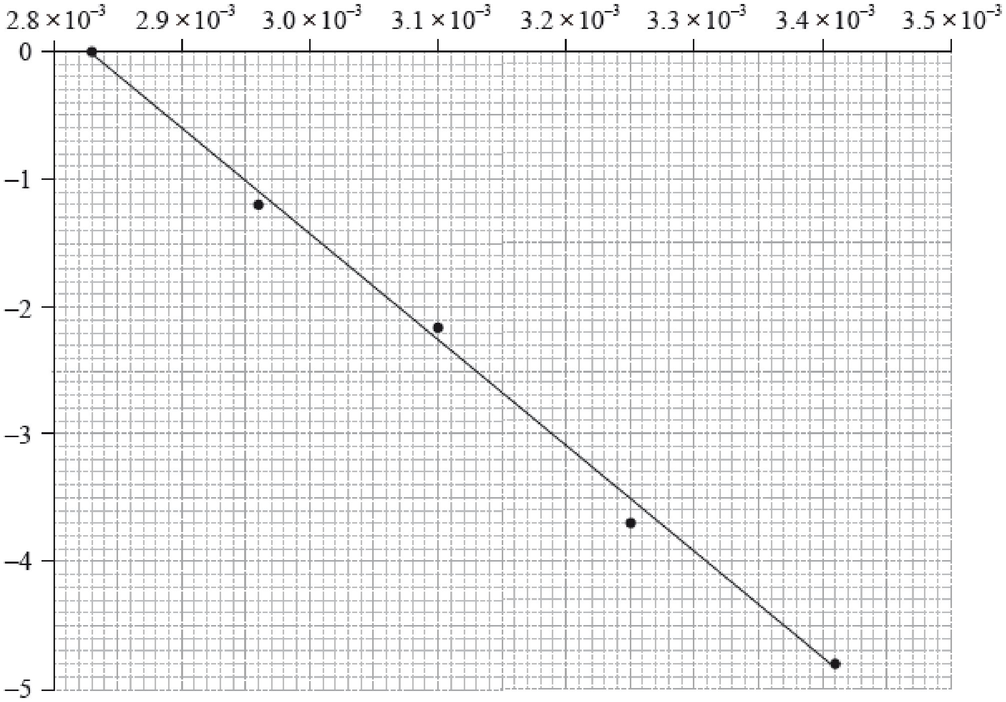
20.0 ± 0.1 $\mathrm{cm^3}$ of 1.00 $\mathrm{mol\,dm^{-3}}$ sulfuric acid (H_2SO_4)

20.0 ± 0.1 $\mathrm{cm^3}$ of 0.0100 $\mathrm{mol\,dm^{-3}}$ sodium thiosulfate ($Na_2S_2O_3$)

50.0 ± 0.1 $\mathrm{cm^3}$ of water with 0.0200 ± 0.0001 g of potassium iodide (KI) dissolved in it.

After 45 seconds this mixture suddenly changed from colourless to blue-black.

The activation energy can be determined using the Arrhenius equation, which is given in Table 1 of the Data Booklet. The experiment was carried out at five different temperatures. An incomplete graph to determine the activation energy of the reaction, based on these results, is shown below.



a. The concentration of iodide ions, I^-, is assumed to be constant. Outline why this is a valid assumption. [1]

b. For this mixture the concentration of hydrogen peroxide, H_2O_2, can also be assumed to be constant. Explain why this is a valid assumption. [2]

c. Explain why the solution suddenly changes colour. [2]

d.i. Calculate the total uncertainty, in $\mathrm{cm^3}$, of the volume of the reaction mixture. [1]

d.ii. Calculate the percentage uncertainty of the concentration of potassium iodide solution added to the overall reaction mixture. [1]

d.iii. Determine the percentage uncertainty in the concentration of potassium iodide in the final reaction solution. [1]

e. The colour change occurs when 1.00×10^{-4} mol of iodine has been formed. Use the total volume of the solution and the time taken, to calculate the rate of the reaction, including appropriate units. [4]

f.i. State the labels for each axis. [2]

x-axis:

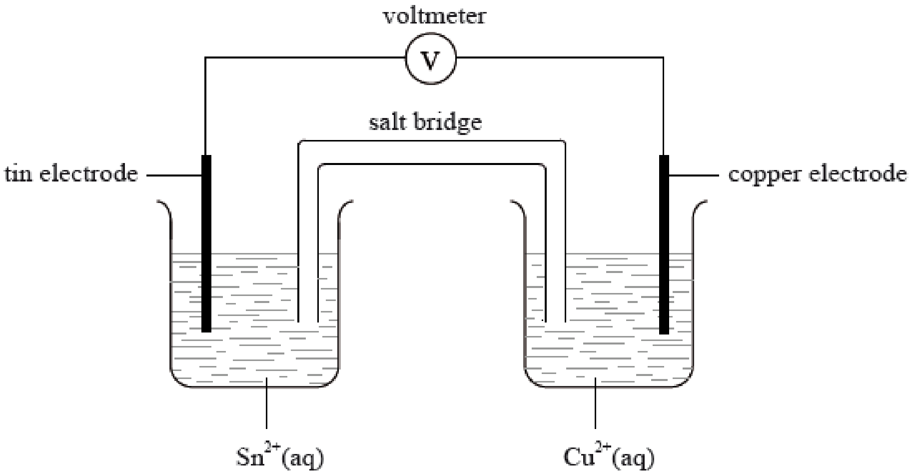
y-axis:

f.ii. Use the graph to determine the activation energy of the reaction, in $\mathrm{kJ\ mol^{-1}}$, correct to **three** significant figures. [3]

g. In another experiment, 0.100 g of a black powder was also added while all other concentrations and volumes remained unchanged. The time taken for the solution to change colour was now 20 seconds. Outline why you think the colour change occurred more rapidly and how you could confirm your hypothesis. [2]

The conditions used in an electrolytic cell can determine the products formed.

A voltaic cell is constructed from two half-cells as illustrated below.



Nitrogen monoxide may be removed from industrial emissions via a reaction with ammonia as shown by the equation below.

$$4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(l)$$

a.i. Draw an electrolytic cell illustrating the electrolysis of molten nickel(II) bromide, $NiBr_2$. Include in the diagram the direction of the electron flow, the polarity of electrodes and state the half-equations for the product formed at each electrode. [5]

a.ii. Deduce the equations for the formation of the major product at the positive electrode (anode) when the following aqueous solutions are electrolysed. [2]

- dilute sodium chloride
- concentrated sodium chloride

b.i. Use Table 14 of the Data Booklet to deduce the equation for the spontaneous reaction occurring in this cell. [1]

b.ii. Calculate the standard potential for this cell. [1]

b.iii. State the conditions necessary for the potential of the cell to equal that calculated in part (b) (ii) using the data from Table 14. [1]

c. Using the data below and data from Table 14 of the Data Booklet, predict and explain which metal, cadmium or chromium, may be obtained by electrolysis of separate aqueous solutions of $\mathrm{Cd^{2+}(aq)}$ ions and $\mathrm{Cr^{2+}(aq)}$ ions. [2]

d.i. Electrolysis is used in the electroplating of metals. The same amount of current is passed through separate aqueous solutions of $\mathrm{NiSO_4}$, $\mathrm{Sn(SO_4)_2}$ and $\mathrm{Cr_2(SO_4)_3}$ in separate electrolytic cells for the same amount of time. State and explain which cell would deposit the greatest amount (in mol) of metal. Identify the electrode at which the metal is deposited. [3]

d.ii. For the $\mathrm{Sn(SO_4)_2}$ cell, suggest **two** factors, other than time and current, that would affect the amount of metal deposited during electroplating. [2]

e.i. Deduce the oxidation number of the nitrogen in the reactants and product. [3]

e.ii. Deduce the oxidation and reduction half-equations and identify the oxidizing agent for the reaction. [3]

e.iii. $30.0\ \mathrm{dm^3}$ of ammonia reacts with $30.0\ \mathrm{dm^3}$ of nitrogen monoxide at 100 °C. Identify which gas is in excess and by how much and calculate the volume of nitrogen produced. [2]

Chemical kinetics involves an understanding of how the molecular world changes with time.

A catalyst provides an alternative pathway for a reaction, lowering the activation energy, E_a.

Sketch graphical representations of the following reactions, for X → products.

For the reaction below, consider the following experimental data.

$$2\mathrm{ClO_2(aq)} + 2\mathrm{OH^-(aq)} \rightarrow \mathrm{ClO_3^-(aq)} + \mathrm{ClO_2^-(aq)} + \mathrm{H_2O(l)}$$

Experiment	**Initial [$\mathrm{ClO_2(aq)}$] / $\mathrm{mol\,dm^{-3}}$**	**Initial [$\mathrm{OH^-(aq)}$] / $\mathrm{mol\,dm^{-3}}$**	**Initial rate / $\mathrm{mol\,dm^{-3}\,s^{-1}}$**
1	1.00×10^{-1}	1.00×10^{-1}	2.30×10^{-1}
2	5.00×10^{-2}	1.00×10^{-1}	5.75×10^{-2}
3	5.00×10^{-2}	3.00×10^{-2}	1.73×10^{-2}

Another reaction involving $\mathrm{OH^-}$ (aq) is the base hydrolysis reaction of an ester.

$$\mathrm{CH_3COOCH_2CH(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{CH_3COO^-(aq)} + \mathrm{CH_3CH_2OH(aq)}$$

A two-step mechanism has been proposed for the following reaction.

$$\begin{array}{ll} \text{Step 1:} & \mathrm{ClO^-(aq)} + \mathrm{ClO^-(aq)} \rightarrow \mathrm{ClO_2^-(aq)} + \mathrm{Cl^-(aq)} \\ \text{Step 2:} & \mathrm{ClO_2^-(aq)} + \mathrm{ClO^-(aq)} \rightarrow \mathrm{ClO_3^-(aq)} + \mathrm{Cl^-(aq)} \end{array}$$

a. (i) Define the term *rate of reaction*. [4]

(ii) Temperature and the addition of a catalyst are two factors that can affect the rate of a reaction. State **two** other factors.

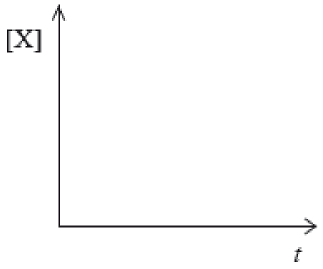
(iii) In the reaction represented below, state **one** method that can be used to measure the rate of the reaction.

$$\mathrm{ClO_3^-(aq) + 5Cl^-(aq) + 6H^+(aq) \rightarrow 3Cl_2(aq) + 3H_2O(l)}$$

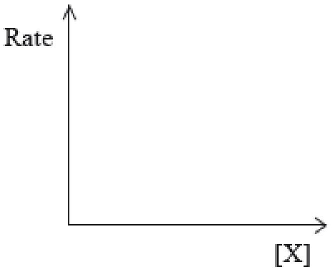
b. (i) Define the term *activation energy*, E_a. [4]

(ii) Sketch the **two** Maxwell–Boltzmann energy distribution curves for a fixed amount of gas at two different temperatures, T_1 and T_2 $(T_2 > T_1)$. Label **both** axes.

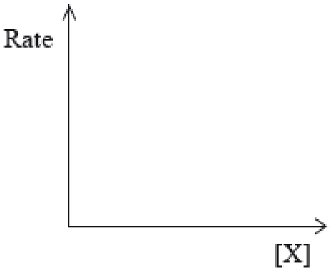
c. (i) Concentration of reactant X against time for a **zero-order** reaction. [3]



(ii) Rate of reaction against concentration of reactant X for a **zero-order** reaction.



(iii) Rate of reaction against concentration of reactant X for a **first-order** reaction.



d. (i) Deduce the rate expression. [5]

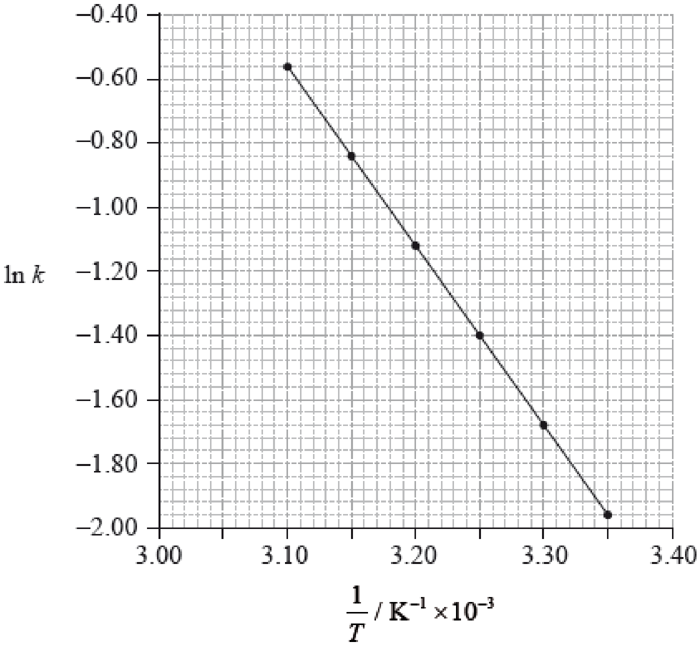
(ii) Determine the rate constant, k, and state its units, using the data from Experiment 2.

(iii) Calculate the rate, in $\mathrm{mol\,dm^{-3}s^{-1}}$, when $[\mathrm{ClO_2(aq)}] = 1.50 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ and $[\mathrm{OH^-(aq)}] = 2.35 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$.

e.i. Apply IUPAC rules to name the ester, $CH_3COOCH_2CH_3$(aq). [1]

e.ii. Describe **qualitatively** the relationship between the rate constant, *k*, and temperature, *T*. [1]

e.iii. The rate of this reaction was measured at different temperatures and the following data were recorded. [4]



Using data from the graph, determine the activation energy, E_a, correct to **three** significant figures and **state its units**.

f.i. Deduce the overall equation for the reaction. [1]

f.ii. Deduce the rate expression for each step. [2]

Step 1:

Step 2:

---

a. Explain why the relative atomic mass of cobalt is greater than the relative atomic mass of nickel, even though the atomic number of nickel is greater than the atomic number of cobalt. [1]

b. Deduce the numbers of protons and electrons in the ion Co^{2+}. [1]

c. Deduce the electron configuration for the ion Co^{2+}. [1]

A student determined the percentage of the active ingredient magnesium hydroxide, $Mg(OH)_2$, in a 1.24 g antacid tablet.

The antacid tablet was added to 50.00 cm^3 of 0.100 mol dm^{-3} sulfuric acid, which was in excess.

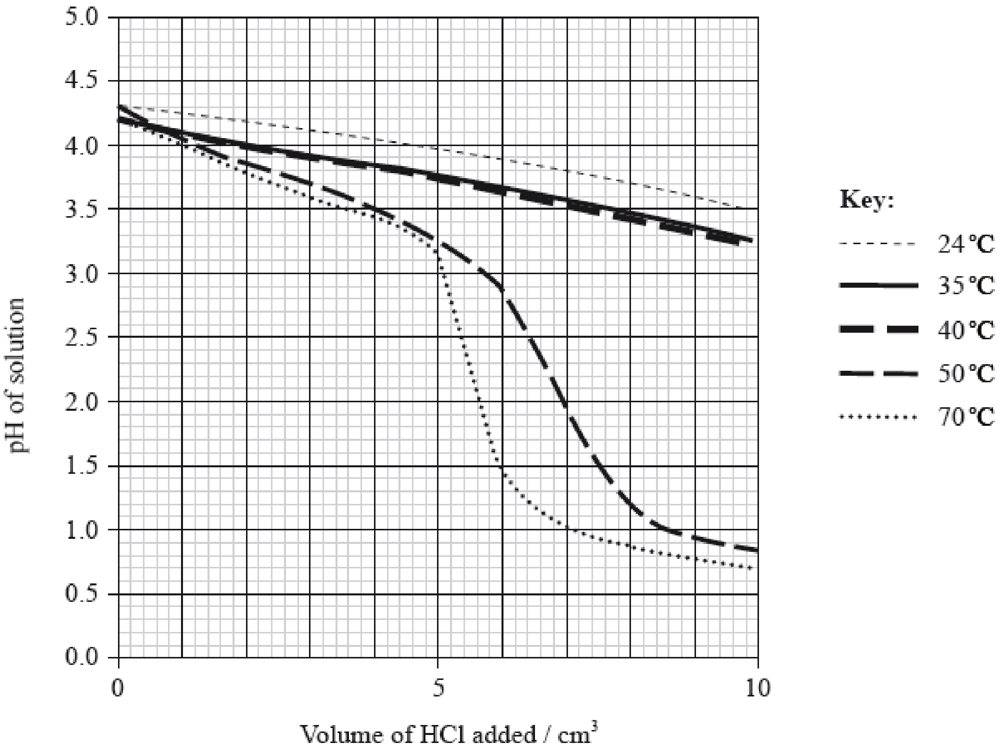
Outline why repeating quantitative measurements is important.

A student decided to determine the molecular mass of a solid monoprotic acid, HA, by titrating a solution of a known mass of the acid.

The following recordings were made.

Mass of bottle / g ± 0.001 g	1.737
Mass of bottle + acid HA / g ± 0.001 g	2.412

To investigate the effect of temperature on the effectiveness of a buffer solution, the student placed 20.0 cm^3 of the buffer solution in a water bath at 24 °C. He added small portions of hydrochloric acid, stirring after each addition, until a total of 10 cm^3 was added, and measured the pH continuously during the addition. The procedure was repeated at different temperatures and the results are shown in the following graph.



d. Determine the molecular formula of HA. [2]

f.i. State what is meant by a *buffer solution*. [2]

f.ii. With reference to the graph on page 4, describe the effect of increasing temperature on the effectiveness of the buffer solution. [2]

Analytical chemistry uses instruments to separate, identify, and quantify matter.

Menthol is an organic compound containing carbon, hydrogen and oxygen.

Nitric oxide reacts with chlorine.

$$2NO\ (g) + Cl_2\ (g) \rightarrow 2NOCl\ (g)$$

The following experimental data were obtained at 101.3 kPa and 263 K.

Experiment	Initial [NO] / mol dm^{-3}	Initial [Cl_2] / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	1.30×10^{-1}	1.30×10^{-1}	3.95×10^{-1}
2	1.30×10^{-1}	2.60×10^{-1}	7.90×10^{-1}
3	2.60×10^{-1}	2.60×10^{-1}	3.16

b. Outline how this spectrum is related to the energy levels in the hydrogen atom. [1]

c. A sample of magnesium has the following isotopic composition. [2]

Isotope	^{24}Mg	^{25}Mg	^{26}Mg
Relative abundance / %	78.6	10.1	11.3

Calculate the relative atomic mass of magnesium based on this data, giving your answer to **two** decimal places.

d.i. Complete combustion of 0.1595 g of menthol produces 0.4490 g of carbon dioxide and 0.1840 g of water. Determine the empirical formula of the compound showing your working. [3]

d.ii. 0.150 g sample of menthol, when vaporized, had a volume of 0.0337 dm^3 at 150 °C and 100.2 kPa. Calculate its molar mass showing your working. [2]

d.iii. Determine the molecular formula of menthol using your answers from parts (d)(i) and (ii). [1]

e.i. Deduce the order of reaction with respect to Cl_2 and NO. [2]

Cl_2:

. . . .

NO:

. . . .

e.ii. State the rate expression for the reaction. [1]

e.iii. Calculate the value of the rate constant at 263 K. [1]

Consider the following sequence of reactions.

$$RCH_3 \xrightarrow{reaction 1} RCH_2Br \xrightarrow{reaction 2} RCH_2OH$$

RCH_3 is an unknown alkane in which R represents an alkyl group.

All the isomers can by hydrolysed with aqueous sodium hydroxide solution. When the reaction of one of these isomers, **X**, was investigated the following kinetic data were obtained.

Experiment	Initial [X] / $mol\,dm^{-3}$	Initial [OH^-] / $mol\,dm^{-3}$	Initial rate of reaction / $mol\,dm^{-3}\,min^{-1}$
1	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{-3}
2	2.0×10^{-2}	4.0×10^{-2}	4.0×10^{-3}
3	4.0×10^{-2}	4.0×10^{-2}	8.0×10^{-3}

a. The alkane contains 82.6% by mass of carbon. Determine its empirical formula, showing your working. [3]

b. A 1.00 g gaseous sample of the alkane has a volume of 385 cm^3 at standard temperature and pressure. Deduce its molecular formula. [2]

c. State the reagent and conditions needed for *reaction 1*. [2]

d. *Reaction 1* involves a free-radical mechanism. Describe the stepwise mechanism, by giving equations to represent the initiation, propagation and termination steps. [4]

e. The mechanism in *reaction 2* is described as S_N2. Explain the mechanism of this reaction using curly arrows to show the movement of electron pairs, and draw the structure of the transition state. [3]

f. There are four structural isomers with the molecular formula C_4H_9Br. One of these structural isomers exists as two optical isomers. Draw diagrams to represent the three-dimensional structures of the two optical isomers. [2]

g. (i) Deduce the rate expression for the reaction. [9]

(ii) Determine the value of the rate constant for the reaction and state its units.

(iii) State the name of isomer **X** and explain your choice.

(iv) State equations for the steps that take place in the mechanism of this reaction and state which of the steps is slow and which is fast.

Phosphorus(V) oxide, P_4O_{10} $(M_r = 283.88)$, reacts vigorously with water $(M_r = 18.02)$, according to the equation below.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

a. A student added 5.00 g of P_4O_{10} to 1.50 g of water. Determine the limiting reactant, showing your working. [2]

b. Calculate the mass of phosphoric(V) acid, H_3PO_4, formed in the reaction. [2]

c. Phosphoric(V) acid, H_3PO_4, has a pK_a of 2.12 (pK_{a1}) while phosphoric(III) acid, H_3PO_3, has a pK_a of 1.23 (pK_{a1}). Identify the weaker of the two acids, giving a reason for your choice. [1]

The element antimony, Sb, is usually found in nature as its sulfide ore, stibnite, Sb_2S_3. This ore was used two thousand years ago by ancient Egyptian women as a cosmetic to darken their eyes and eyelashes.

Antimony contains two stable isotopes, $^{121}\mathrm{Sb}$ and $^{123}\mathrm{Sb}$. The relative atomic mass of antimony is given in Table 5 of the Data Booklet.

a.i. Calculate the percentage by mass of antimony in a sample of pure stibnite. State your answer to **four** significant figures. [2]

c.i. Calculate the percentage of each isotope in pure antimony. State your answers to **three** significant figures. [2]

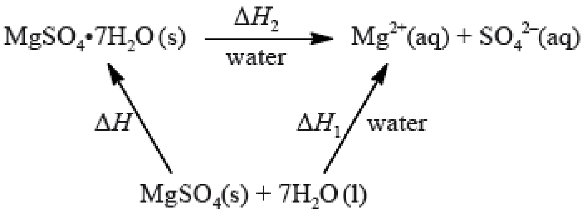
c.iii State the number of neutrons present in an atom of $^{121}\mathrm{Sb}$. [1]

Two chemistry students wished to determine the enthalpy of hydration of anhydrous magnesium sulfate. They measured the initial and the highest temperature reached when anhydrous magnesium sulfate, $\mathrm{MgSO_4(s)}$, was dissolved in water. They presented their results in the table below.

mass of anhydrous magnesium sulfate / g	3.01
volume of water / $\mathrm{cm^3}$	50.0
initial temperature / °C	17.0
highest temperature / °C	26.7

The students repeated the experiment using 6.16 g of solid hydrated magnesium sulfate, $\mathrm{MgSO_4 \bullet 7H_2O(s)}$, and $50.0\ \mathrm{cm^3}$ of water. They found the enthalpy change, ΔH_2 , to be $+18\ \mathrm{kJ\ mol^{-1}}$.

The enthalpy of hydration of solid anhydrous magnesium sulfate is difficult to determine experimentally, but can be determined using the diagram below.



a. (i) Calculate the amount, in mol, of anhydrous magnesium sulfate. [2]

(ii) Calculate the enthalpy change, ΔH_1, for anhydrous magnesium sulfate dissolving in water, in $\mathrm{kJ\ mol^{-1}}$. State your answer to the correct number of significant figures.

b. (i) Determine the enthalpy change, ΔH, in $\mathrm{kJ\ mol^{-1}}$, for the hydration of solid anhydrous magnesium sulfate, $\mathrm{MgSO_4}$. [2]

(ii) The literature value for the enthalpy of hydration of anhydrous magnesium sulfate is $-103\ \mathrm{kJ\ mol^{-1}}$. Calculate the percentage difference between the literature value and the value determined from experimental results, giving your answer to **one** decimal place. (If you did not obtain an answer for the experimental value in (b)(i) then use the value of $-100\ \mathrm{kJ\ mol^{-1}}$, but this is **not** the correct value.)

c. Another group of students experimentally determined an enthalpy of hydration of $-95\ \mathrm{kJ\ mol^{-1}}$. Outline two reasons which may explain the variation between the experimental and literature values. [2]

d. Magnesium sulfate is one of the products formed when acid rain reacts with dolomitic limestone. This limestone is a mixture of magnesium carbonate and calcium carbonate. [6]

(i) State the equation for the reaction of sulfuric acid with magnesium carbonate.

(ii) Deduce the Lewis (electron dot) structure of the carbonate ion, giving the shape and the oxygen-carbon-oxygen bond angle.

Lewis (electron dot) structure:

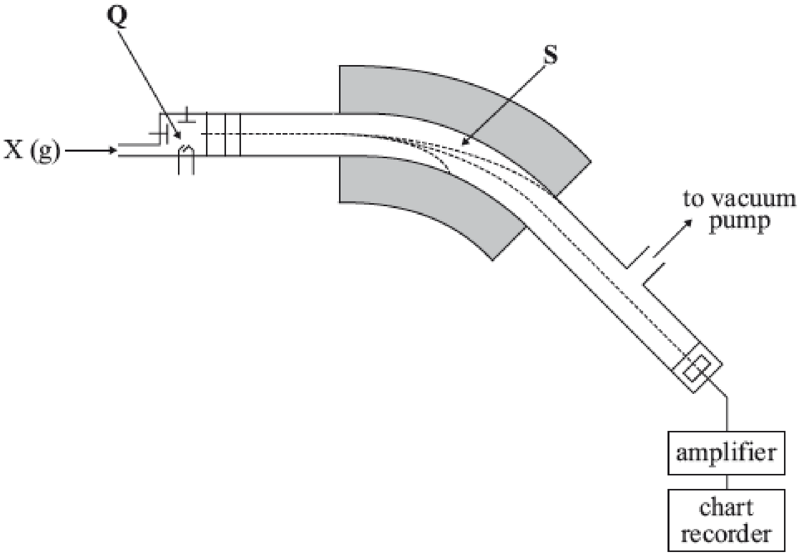
Shape:

Bond angle:

(iii) There are three possible Lewis structures that can be drawn for the carbonate ion, which lead to a resonance structure. Explain, with reference to the electrons, why all carbon-oxygen bonds have the same length.

(iv) Deduce the hybridization of the carbon atom in the carbonate ion.

Magnesium has three stable isotopes, $^{24}\mathrm{Mg}$, $^{25}\mathrm{Mg}$ and $^{26}\mathrm{Mg}$. The relative abundance of each isotope is 78.99%, 10.00% and 11.01%, respectively, and can be determined using a mass spectrometer.



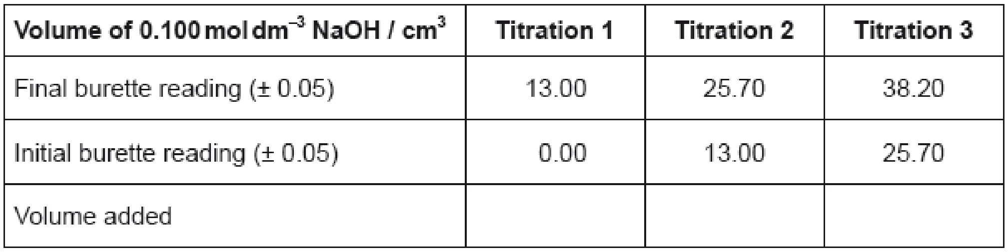
Calculate, showing your working, the relative atomic mass, A_r, of magnesium, giving your answer to two decimal places.

Ethanedioic acid is a diprotic acid. A student determined the value of x in the formula of hydrated ethanedioic acid, $\mathrm{HOOC{-}COOH \bullet xH_2O}$, by titrating a known mass of the acid with a 0.100 $\mathrm{mol\,dm^{-3}}$ solution of NaOH(aq).

0.795 g of ethanedioic acid was dissolved in distilled water and made up to a total volume of 250 $\mathrm{cm^3}$ in a volumetric flask.

$25\ \mathrm{cm^3}$ of this ethanedioic acid solution was pipetted into a flask and titrated against aqueous sodium hydroxide using phenolphthalein as an indicator.

The titration was then repeated twice to obtain the results below.



Volume of 0.100 mol $\mathrm{dm^{-3}}$ NaOH / $\mathrm{cm^3}$	**Titration 1**	**Titration 2**	**Titration 3**
Final burette reading (± 0.05)	13.00	25.70	38.20
Initial burette reading (± 0.05)	0.00	13.00	25.70
Volume added			

a. Calculate the average volume of NaOH added, in $\mathrm{cm^3}$, in titrations 2 and 3, and then calculate the amount, in mol, of NaOH added. [2]

b.i. The equation for the reaction taking place in the titration is: [1]

$$\mathrm{HOOC{-}COOH(aq) + 2NaOH(aq) \rightarrow NaOOC{-}COONa(aq) + 2H_2O(l)}$$

Determine the amount, in mol, of ethanedioic acid that reacts with the average

volume of NaOH(aq).

b.ii. Determine the amount, in mol, of ethanedioic acid present in $250\ \mathrm{cm^3}$ of the original solution. [1]

b.iii. Determine the molar mass of hydrated ethanedioic acid. [1]

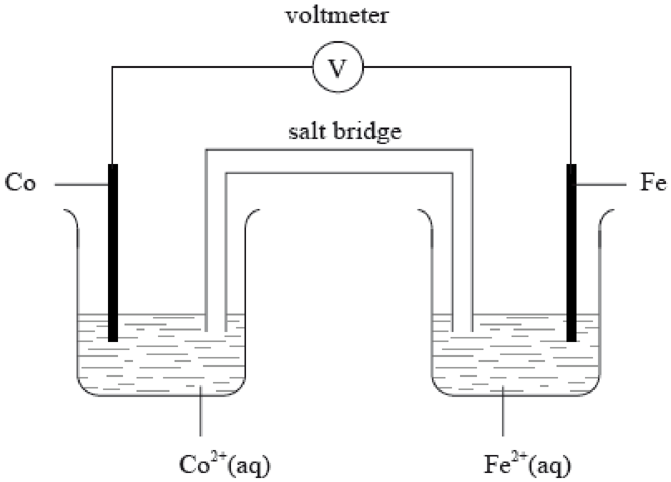
b.iv. Determine the value of x in the formula $\mathrm{HOOC{-}COOH \bullet xH_2O}$. [2]

c. Identify the strongest intermolecular force in solid ethanedioic acid. [1]

d. Deduce the Lewis (electron dot) structure of ethanedioic acid, $\mathrm{HOOC{-}COOH}$. [1]

e. Predict and explain the difference in carbon-oxygen bond lengths in ethanedioic acid and its conjugate base, $\mathrm{^{-}OOC{-}COO^{-}}$. [3]

An electrochemical cell is made from an iron half-cell connected to a cobalt half-cell:



The standard electrode potential for $\mathrm{Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)}$ is –0.45 V. The total cell potential obtained when the cell is operating under standard conditions is 0.17 V. Cobalt is produced during the spontaneous reaction.

An electrolytic cell is made using a very dilute solution of sodium chloride.

Predict the products by giving the relevant half-equation for the reaction occurring at each electrode if the electrolyte of the cell described in part (c) was changed to:

a.i. Define the term *standard electrode potential* and state the meaning of the minus sign in the value of –0.45 V. [3]

a.ii. Calculate the value for the standard electrode potential for the cobalt half-cell. [1]

a.iii. Deduce which species acts as the oxidizing agent when the cell is operating. [1]

a.iv. Deduce the equation for the spontaneous reaction taking place when the iron half-cell is connected instead to an aluminium half-cell. [2]

a.v. Explain the function of the salt bridge in an electrochemical cell. [2]

b.i. $\mathrm{[Co(H_2O)_6]^{2+}}$ [1]

b.ii. $\mathrm{Co_2(SO_4)_3}$ [1]

b.iii. $\mathrm{[CoCl_4]^{2-}}$ [1]

c.i. Draw a labelled diagram of the cell. Use an arrow to show the direction of the electron flow and identify the positive and negative electrodes. [3]

c.ii. Give the formulas of all the ions present in the solution. [2]

c.iii. Predict the products obtained at each electrode and state the half-equation for the formation of each product. [3]

c.iv. Deduce the molar ratios of the products obtained at the two electrodes. [1]

d.i. concentrated sodium chloride [2]

d.ii. molten sodium bromide [2]

A class studied the equilibrium established when ethanoic acid and ethanol react together in the presence of a strong acid, using propanone as an inert solvent. The equation is given below.

$$\mathrm{CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O}$$

One group made the following **initial mixture**:

Liquid	Volume / cm^3
Ethanoic acid	5.00 ± 0.05
Ethanol	5.00 ± 0.05
$6.00\ mol\,dm^{-3}$ aqueous hydrochloric acid	1.00 ± 0.02
Propanone	39.0 ± 0.5

After one week, a $5.00 \pm 0.05\ \mathrm{cm^3}$ sample of the final equilibrium mixture was pipetted out and titrated with $0.200\ \mathrm{mol\,dm^{-3}}$ aqueous sodium hydroxide to determine the amount of ethanoic acid remaining. The following titration results were obtained:

Titration number	1	2	3
Initial reading / $cm^3 \pm 0.05$	1.20	0.60	14.60
Final reading / $cm^3 \pm 0.05$	28.80	26.50	40.70
Titre / cm^3	27.60	25.90	26.10

a. The density of ethanoic acid is $1.05\ \mathrm{g\,cm^{-3}}$. Determine the amount, in mol, of ethanoic acid present in the initial mixture. [3]

b. The concentration of ethanoic acid can be calculated as $1.748\ \mathrm{mol\,dm^{-3}}$. Determine the percentage uncertainty of this value. (Neglect any uncertainty in the density and the molar mass.) [3]

c.i. Calculate the absolute uncertainty of the titre for Titration 1 ($27.60\ \mathrm{cm^3}$). [1]

c.ii. Suggest the average volume of alkali, required to neutralize the $5.00\ \mathrm{cm^3}$ sample, that the student should use. [1]

c.iii. $3.00\ \mathrm{cm^3}$ of the $0.200\ \mathrm{mol\,dm^{-3}}$ aqueous sodium hydroxide reacted with the hydrochloric acid present in the $5.00\ \mathrm{cm^3}$ sample. Determine the concentration of ethanoic acid in the final equilibrium mixture. [2]

c.iv. Deduce the equilibrium constant expression for the reaction. [1]

c.v. The other concentrations in the equilibrium mixture were calculated as follows: [1]

Compound	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Concentration / $mol\ dm^{-3}$	0.884	0.828	1.80

Use these data, along with your answer to part (iii), to determine the value of the equilibrium constant. (If you did not obtain an answer to part (iii), assume the concentrations of ethanol and ethanoic acid are equal, although this is not the case.)

d. Outline how you could establish that the system had reached equilibrium at the end of one week. [1]

e. Outline why changing the temperature has only a very small effect on the value of the equilibrium constant for this equilibrium. [1]

f. Outline how adding some ethyl ethanoate to the initial mixture would affect the amount of ethanoic acid converted to product. [2]

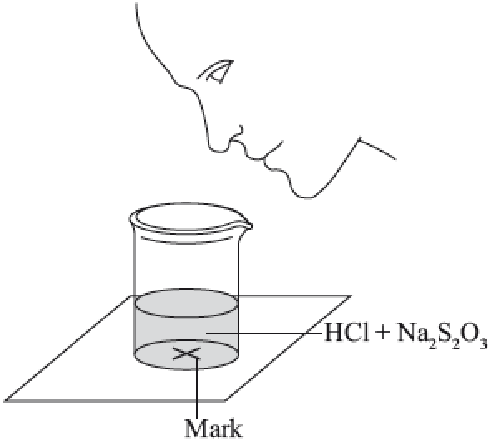
g. Propanone is used as the solvent because one compound involved in the equilibrium is insoluble in water. Identify this compound and explain why it is insoluble in water. [2]

h. Suggest **one** other reason why using water as a solvent would make the experiment less successful. [1]

A group of students investigated the rate of the reaction between aqueous sodium thiosulfate and hydrochloric acid according to the equation below.

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$$

The two reagents were rapidly mixed together in a beaker and placed over a mark on a piece of paper. The time taken for the precipitate of sulfur to obscure the mark when viewed through the reaction mixture was recorded.



Initially they measured out $10.0\ cm^3$ of $0.500\ mol\ dm^{-3}$ hydrochloric acid and then added $40.0\ cm^3$ of $0.0200\ mol\ dm^{-3}$ aqueous sodium thiosulfate. The mark on the paper was obscured 47 seconds after the solutions were mixed.

One proposed mechanism for this reaction is:

$S_2O_3^{2-}(aq) + H^+(aq) \rightleftharpoons HS_2O_3^-(aq)$ Fast

$HS_2O_3^-(aq) + H^+(aq) \rightarrow SO_2(g) + S(s) + H_2O(l)$ Slow

The teacher asked the students to devise another technique to measure the rate of this reaction.

Another group suggested collecting the sulfur dioxide and drawing a graph of the volume of gas against time.

a. (i) State the volumes of the liquids that should be mixed. [3]

Liquid	$0.500\ mol\ dm^{-3}\ HCl$	$0.0200\ mol\ dm^{-3}\ Na_2S_2O_3$	Water
Volume / cm^3			

(ii) State why it is important that the students use a similar beaker for both reactions.

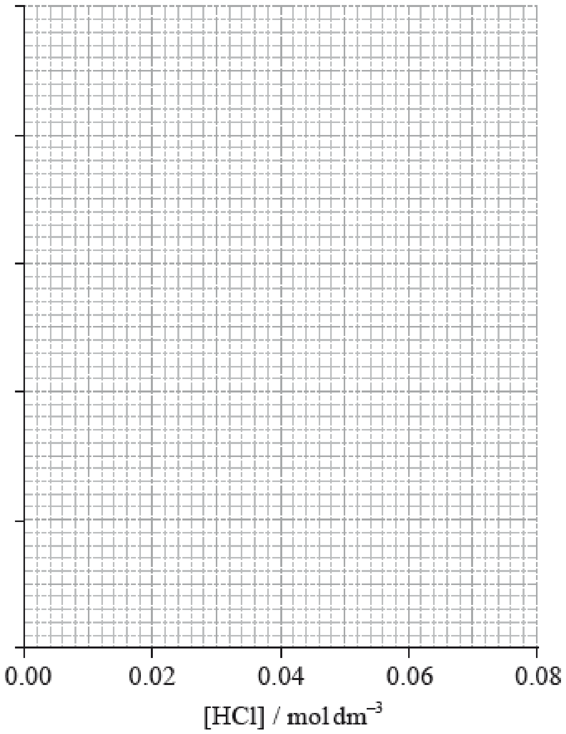
(iii) If the reaction were first order with respect to the thiosulfate ion, predict the time it would take for the mark on the paper to be obscured when the concentration of sodium thiosulfate solution is halved.

b. (i) Deduce the rate expression of this mechanism. [6]

(ii) The results of an experiment investigating the effect of the concentration of hydrochloric acid on the rate, while keeping the concentration of thiosulfate at the original value, are given in the table below.

[HCl] / mol dm^{-3}	0.020	0.040	0.060	0.080
Time / s	89.1	72.8	62.4	54.2

On the axes provided, draw an appropriate graph to investigate the order of the reaction with respect to hydrochloric acid.



(iii) Identify **two** ways in which these data **do not** support the rate expression deduced in part (i).

c. (i) Sketch and label, indicating an approximate activation energy, the Maxwell–Boltzmann energy distribution curves for two temperatures, T_1 [6]

and $T2$ $(T_2 > T_1)$, at which the rate of reaction would be significantly different.

(ii) Explain why increasing the temperature of the reaction mixture would significantly increase the rate of the reaction.

d. (i) One group suggested recording how long it takes for the pH of the solution to change by one unit. Calculate the initial pH of the original reaction mixture. [3]

(ii) Deduce the percentage of hydrochloric acid that would have to be used up for the pH to change by one unit.

e.i. Calculate the volume of sulfur dioxide, in cm^3, that the original reaction mixture would produce if it were collected at $1.00 \times 10^5\ \mathrm{Pa}$ and 300 K. [3]

e.ii. Sulfur dioxide, a major cause of acid rain, is quite soluble in water and the equilibrium shown below is established. [3]

$$\mathrm{SO_2(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H^+(aq)}$$

Given that the K_a for this equilibrium is $1.25 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$, determine the pH of a $2.00\ \mathrm{mol\,dm^{-3}}$ solution of sulfur dioxide.

e.iii Using Table 15 of the Data Booklet, identify an organic acid that is a stronger acid than sulfur dioxide. [1]

Magnesium is a group 2 metal which exists as a number of isotopes and forms many compounds.

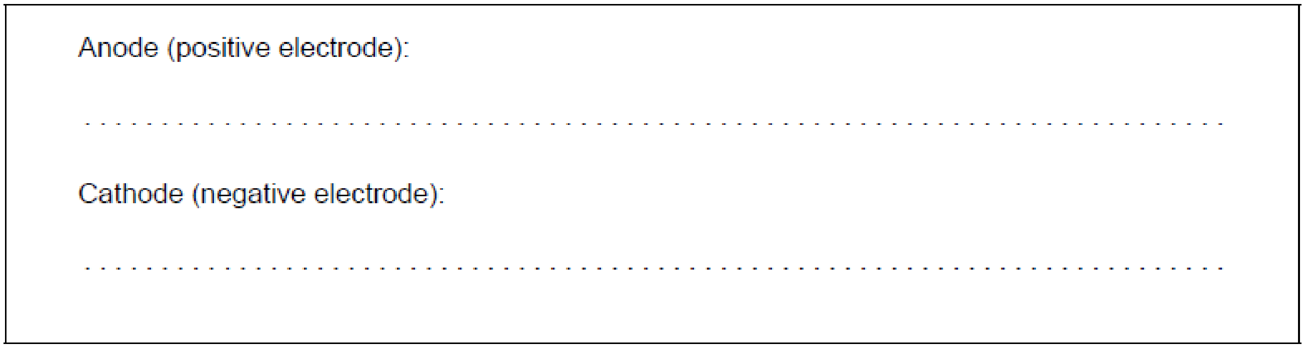
c. Magnesium ions produce no emission or absorption lines in the visible region of the electromagnetic spectrum. Suggest why most magnesium compounds tested in a school laboratory show traces of yellow in the flame. [1]

d. (i) Explain the convergence of lines in a hydrogen emission spectrum. [2]

(ii) State what can be determined from the frequency of the convergence limit.

i. Magnesium chloride can be electrolysed. [5]

(i) Deduce the half-equations for the reactions at each electrode when **molten** magnesium chloride is electrolysed, showing the state symbols of the products. The melting points of magnesium and magnesium chloride are 922K and 987K respectively.



Anode (positive electrode):

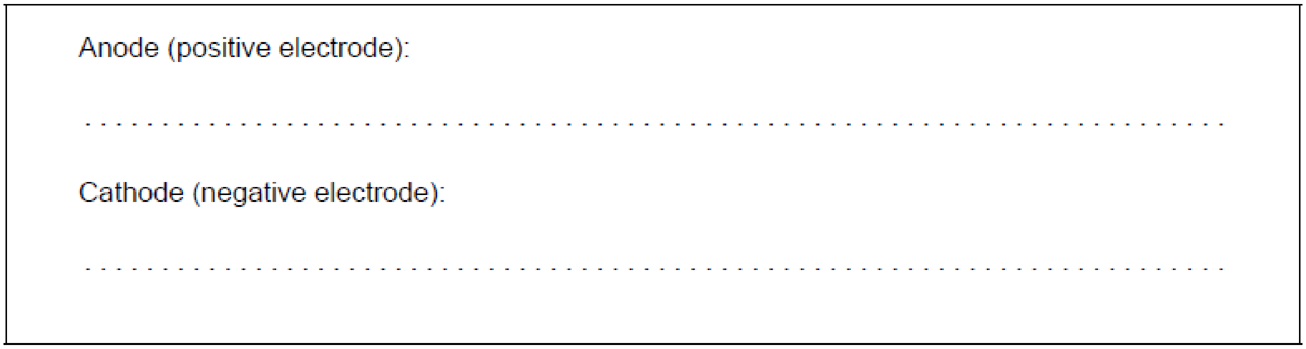
. . . .

Cathode (negative electrode):

. . . .

(ii) Identify the type of reaction occurring at the cathode (negative electrode).

(iii) State the products when a very **dilute** aqueous solution of magnesium chloride is electrolysed.



Anode (positive electrode):

. . . .

Cathode (negative electrode):

. . . .

j. Standard electrode potentials are measured relative to the standard hydrogen electrode. Describe a standard hydrogen electrode. [2]

k. A magnesium half-cell, Mg(s)/Mg^{2+}(aq), can be connected to a copper half-cell, Cu(s)/Cu^{2+}(aq). [4]

(i) Formulate an equation for the spontaneous reaction that occurs when the circuit is completed.

(ii) Determine the standard cell potential, in V, for the cell. Refer to section 24 of the data booklet.

(iii) Predict, giving a reason, the change in cell potential when the concentration of copper ions increases.

$25.0\ \mathrm{cm}^3$ of $0.200\ \mathrm{mol\,dm^{-3}}$ ethanoic acid was added to $30.0\ \mathrm{cm}^3$ of a $0.150\ \mathrm{mol\,dm^{-3}}$ sodium hydrogencarbonate solution, $\mathrm{NaHCO_3(aq)}$.

The molar mass of a volatile organic liquid, **X**, can be determined experimentally by allowing it to vaporize completely at a controlled temperature and pressure. 0.348 g of **X** was injected into a gas syringe maintained at a temperature of 90 °C and a pressure of $1.01 \times 10^5\ \mathrm{Pa}$. Once it had reached equilibrium, the gas volume was measured as $95.0\ \mathrm{cm}^3$.

Bromoethane, $\mathrm{CH_3CH_2Br}$, undergoes a substitution reaction to form ethylamine, $\mathrm{CH_3CH_2NH_2}$.

Many organic compounds exist as stereoisomers.

a. Outline how electrical conductivity can be used to distinguish between a $0.200\ \mathrm{mol\,dm^{-3}}$ solution of ethanoic acid, $\mathrm{CH_3COOH}$, and a $0.200\ \mathrm{mol\,dm^{-3}}$ solution of hydrochloric acid, HCl. [1]

b. (i) State an equation for the reaction of ethanoic acid with a solution of sodium hydrogencarbonate. [5]

(ii) Determine which is the limiting reagent. Show your working.

(iii) Calculate the mass, in g, of carbon dioxide gas produced.

c. (i) Determine the amount, in mol, of **X** in the gas syringe. [4]

(ii) Calculate the molar mass of **X**.

d.i. Deduce the mechanism for the reaction using equations and curly arrows to represent the movement of electron pairs. [3]

e. (i) Outline the meaning of the term *stereoisomers*. [6]

(ii) Draw the structures of the two stereoisomers of dichloroethene, $C_2H_2Cl_2$.

(iii) Explain why this type of stereoisomerism exists in $C_2H_2Cl_2$.

(iv) Draw the structures of the two stereoisomers of 1-chloro-1-fluoroethane, C_2H_4FCl, showing the relationship between them.

(v) Outline how the two isomers of C_2H_4FCl could be distinguished from each other.

Phosphine (IUPAC name phosphane) is a hydride of phosphorus, with the formula PH_3.

a. (i) Draw a Lewis (electron dot) structure of phosphine. [8]

(ii) State the hybridization of the phosphorus atom in phosphine.

(iii) Deduce, giving your reason, whether phosphine would act as a Lewis acid, a Lewis base, or neither.

(iv) Outline whether you expect the bonds in phosphine to be polar or non-polar, giving a brief reason.

(v) Phosphine has a much greater molar mass than ammonia. Explain why phosphine has a significantly lower boiling point than ammonia.

(vi) Ammonia acts as a weak Brønsted–Lowry base when dissolved in water.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Outline what is meant by the terms “weak” and “Brønsted–Lowry base”.

Weak:

Brønsted–Lowry base:

b. Phosphine is usually prepared by heating white phosphorus, one of the allotropes of phosphorus, with concentrated aqueous sodium hydroxide. The equation for the reaction is: [8]

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

(i) The first reagent is written as P_4, not 4P. Describe the difference between P_4 and 4P.

(ii) The ion $H_2PO_2^-$ is amphiprotic. Outline what is meant by amphiprotic, giving the formulas of **both** species it is converted to when it behaves in this manner.

(iii) State the oxidation state of phosphorus in P_4 and $H_2PO_2^-$.

P_4:

$H_2PO_2^-$:

(iv) Oxidation is now defined in terms of change of oxidation number. Explore how earlier definitions of oxidation and reduction may have led to conflicting answers for the conversion of P_4 to $H_2PO_2^-$ and the way in which the use of oxidation numbers has resolved this.

c. 2.478 g of white phosphorus was used to make phosphine according to the equation: [4]

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

(i) Calculate the amount, in mol, of white phosphorus used.

(ii) This phosphorus was reacted with 100.0 cm^3 of 5.00 mol dm^{-3} aqueous sodium hydroxide. Deduce, showing your working, which was the limiting reagent.

(iii) Determine the excess amount, in mol, of the other reagent.

(iv) Determine the volume of phosphine, measured in cm^3 at standard temperature and pressure, that was produced.

d. Impurities cause phosphine to ignite spontaneously in air to form an oxide of phosphorus and water. [9]

(i) 200.0 g of air was heated by the energy from the complete combustion of 1.00 mol phosphine. Calculate the temperature rise using section 1 of the data booklet and the data below.

Standard enthalpy of combustion of phosphine, $\Delta H_c^\ominus = -750\,kJ\,mol^{-1}$

Specific heat capacity of air = $1.00 J g^{-1} K^{-1} = 1.00 kJ kg^{-1} K^{-1}$

(ii) The oxide formed in the reaction with air contains 43.6% phosphorus by mass. Determine the empirical formula of the oxide, showing your method.

(iii) The molar mass of the oxide is approximately 285 g mol^{-1}. Determine the molecular formula of the oxide.

(iv) State the equation for the reaction of this oxide of phosphorus with water.

(v) Suggest why oxides of phosphorus are not major contributors to acid deposition.

(vi) The levels of sulfur dioxide, a major contributor to acid deposition, can be minimized by either pre-combustion and post-combustion methods. Outline **one** technique of each method.

Pre-combustion:

Post-combustion:

Vanadium has a number of different oxidation states.

Electrode potentials for the reactions of vanadium and other species are shown below.

$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	$-0.26\,V$
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	$+0.34\,V$
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	$+1.0\,V$

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	$-0.76\,V$
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	$-0.13\,V$
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	$+0.17\,V$
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	$+0.80\,V$
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	$+1.36\,V$

a. Determine the oxidation state of vanadium in each of the following species. [2]

V_2O_5:

. . . .

VO^{2+}:

. . . .

b.i. Identify, from the table, a non-vanadium species that can reduce $VO^{2+}(aq)$ to $V^{3+}(aq)$ but no further. [1]

b.ii. Identify, from the table, a non-vanadium species that could convert $VO_2^+(aq)$ to $V^{2+}(aq)$. [1]

c.i. Formulate an equation for the reaction between $VO^{2+}(aq)$ and $V^{2+}(aq)$ in acidic solution to form $V^{3+}(aq)$. [1]

c.ii. Comment on the spontaneity of this reaction by calculating a value for ΔG^θ using the data given in (b) and in section 1 of the data booklet. [3]

This question is about carbon and chlorine compounds.

a. Ethane, C_2H_6, reacts with chlorine in sunlight. State the type of this reaction and the name of the mechanism by which it occurs. [1]

Type of reaction:

. . . .

Mechanism:

. . . .

b.i. Formulate equations for the two propagation steps and one termination step in the formation of chloroethane from ethane. [3]

Two propagation steps:

. . . .

. . . .

. . . .

. . . .

One termination step:

. . . .

. . . .

b.ii. Deduce the splitting patterns in the ^1H NMR spectrum of C_2H_5Cl. [1]

b.iii. Explain why tetramethylsilane (TMS) is often used as a reference standard in ^1H NMR. [2]

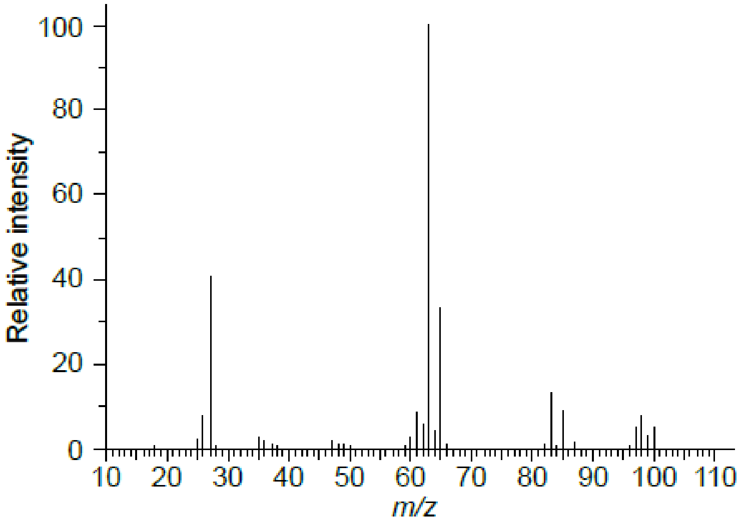
c.i. One possible product, **X**, of the reaction of ethane with chlorine has the following composition by mass: [2]

carbon: 24.27%, hydrogen: 4.08%, chlorine: 71.65%

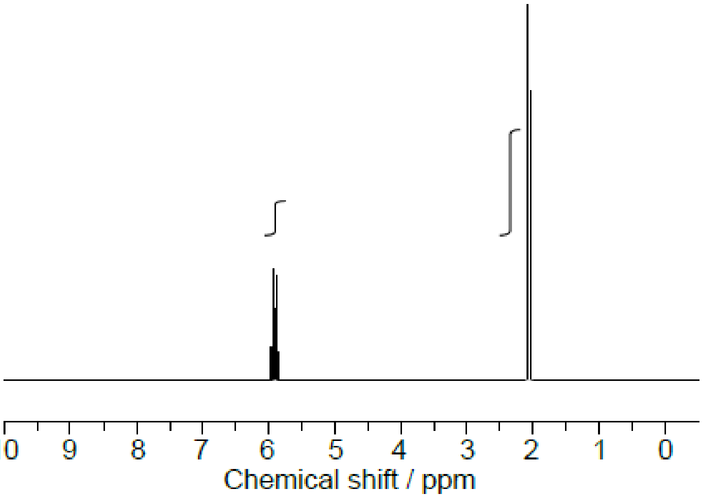
Determine the empirical formula of the product.

c.ii. The mass and ^1H NMR spectra of product **X** are shown below. Deduce, giving your reasons, its structural formula and hence the name of the compound. [3]

Mass spectrum:



^{1}H NMR spectrum:



[Source: http://sdbs.db.aist.go.jp]

c.iii When the product **X** is reacted with NaOH in a hot alcoholic solution, C_2H_3Cl is formed. State the role of the reactant NaOH other than as a nucleophile. [1]

d. Chloroethene, C_2H_3Cl, can undergo polymerization. Draw a section of the polymer with three repeating units. [1]