HL Paper 2

Enthalpy changes depend on the number and type of bonds broken and formed.

The table lists the standard enthalpies of formation, $\Delta H_f^\ominus$, for some of the species in the reaction above.

	CH_4 (g)	H_2O (g)	CO (g)	H_2 (g)
$\Delta H_f^\ominus$ / kJ mol^{-1}	−74.0	−242	−111	

Enthalpy changes depend on the number and type of bonds broken and formed.

a. Hydrogen gas can be formed industrially by the reaction of natural gas with steam. [3]

$$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$$

Determine the enthalpy change, Δ*H,* for the reaction, in kJ, using section 11 of the data booklet.

Bond enthalpy for C≡O: 1077 kJ mol^{-1}

b.i. Outline why no value is listed for H_2(g). [1]

b.ii. Determine the value of $\Delta H^\ominus$, in kJ, for the reaction using the values in the table. [1]

c. The table lists standard entropy, $S^\ominus$, values. [1]

	CH_4 (g)	H_2O (g)	CO (g)	H_2 (g)
$S^\ominus$ / J K^{-1} mol^{-1}	+186	+189	+198	+131

Calculate the standard entropy change for the reaction, $\Delta S^\ominus$, in J K^{-1}.

$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

d. Calculate the standard free energy change, $\Delta G^\ominus$, in kJ, for the reaction at 298 K using your answer to (b)(ii). [1]

e. Determine the temperature, in K, above which the reaction becomes spontaneous. [1]

Consider the reaction:

$$\mathrm{CuS(s) + H_2(g) \rightarrow Cu(s) + H_2S(g)}$$

Given:

	H_2S (g)	CuS (s)
$\Delta G_f^\ominus$ / kJ mol^{-1}	−33.6	−53.6
$\Delta H_f^\ominus$ / kJ mol^{-1}	−20.6	−53.1

a. Deduce and explain the sign of the entropy change for the following reaction. [2]

$$\mathrm{CO(g) + 2H_2(g) \rightarrow CH_3OH(l)}$$

b.i. Suggest why the ΔH_f^Θ values for $\mathrm{H_2(g)}$ and Cu(s) are not given in the table. [1]

b.ii. Determine the standard enthalpy change at 298 K for the reaction. [1]

b.iii. Determine the standard free energy change at 298 K for the reaction. Deduce whether or not the reaction is spontaneous at this temperature. [2]

b.iv. Determine the standard entropy change at 298 K for the reaction. [1]

b.v. Estimate the temperature, in K, at which the standard change in free energy equals zero. You should assume that the values of the standard enthalpy and entropy changes are not affected by the change in temperature. [1]

An example of a homogeneous reversible reaction is the reaction between hydrogen and iodine.

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

Propene can be hydrogenated in the presence of a nickel catalyst to form propane. Use the data below to answer the questions that follow.

Compound	Formula	ΔH^Θ_f / kJ mol^{-1}	S^Θ / J K^{-1} mol^{-1}
hydrogen	$H_2(g)$	0	+131
propane	$C_3H_8(g)$	−104	+270
propene	$C_3H_6(g)$	+20.4	+267

a.v. At a temperature just above 700 K it is found that when 1.60 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium in a $4.00\ \mathrm{dm^3}$ flask, the amount of hydrogen iodide formed in the equilibrium mixture is 1.80 mol. Determine the value of the equilibrium constant at this temperature. [4]

b.i. Outline why the value for the standard enthalpy change of formation of hydrogen is zero. [1]

b.ii. Calculate the standard enthalpy change for the hydrogenation of propene. [2]

b.iii. Calculate the standard entropy change for the hydrogenation of propene. [2]

b.iv. Determine the value of ΔG^Θ for the hydrogenation of propene at 298 K. [2]

b.v. At 298 K the hydrogenation of propene is a spontaneous process. Determine the temperature above which propane will spontaneously decompose into propene and hydrogen. [2]

The photochemical chlorination of methane can occur at low temperature.

The overall equation for monochlorination of methane is:

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

Calculate the standard enthalpy change for the reaction, ΔH^θ, using section 12 of the data booklet.

The reaction between ethene and steam is used in the industrial production of ethanol.

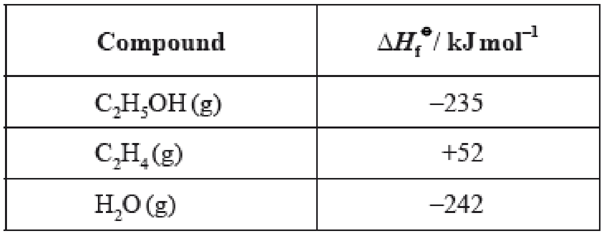
$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

The enthalpy change of the reaction can be calculated either by using average bond enthalpies or by using standard enthalpies of formation.

a. Determine the enthalpy change of the reaction, in $\mathrm{kJ\,mol^{-1}}$, using the average bond enthalpies in Table 10 of the Data Booklet. [3]

b. (i) Define the term *standard enthalpy change of formation*. [4]

(ii) Determine the enthalpy change of the reaction, in $\mathrm{kJ\,mol^{-1}}$, between ethene and steam using the enthalpy change of formation values given below.



Compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
$C_2H_5OH(g)$	–235
$C_2H_4(g)$	+52
$H_2O(g)$	–242

c. Comment on which of the values obtained in (a) and (b)(ii) is more accurate, giving a reason. [1]

d. Predict the sign of the entropy change of the reaction, ΔS, giving a reason. [1]

To determine the enthalpy change of combustion of methanol, CH_3OH, 0.230 g of methanol was combusted in a spirit burner. The heat released increased the temperature of $50.0\ \mathrm{cm^3}$ of water from 24.5 °C to 45.8 °C.

Methanol can be produced according to the following equation.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

The manufacture of gaseous methanol from CO and H_2 involves an equilibrium reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H^\ominus < 0$$

b.i. Calculate the standard enthalpy change of this reaction, using the values of enthalpy of combustion in Table 12 of the Data Booklet. [3]

b.ii. Calculate the standard entropy change for this reaction, $\Delta S^{\ominus}$, using Table 11 of the Data Booklet and given: [1]

$S^{\ominus}(\text{CO}) = 198\ \text{J K}^{-1}\text{mol}^{-1}$ and $S^{\ominus}(\text{H}_2) = 131\ \text{J K}^{-1}\text{mol}^{-1}$.

b.iii. Calculate, stating units, the standard free energy change for this reaction, $\Delta G^{\ominus}$, at 298 K. [2]

b.iv. Predict, with a reason, the effect of an increase in temperature on the spontaneity of this reaction. [3]

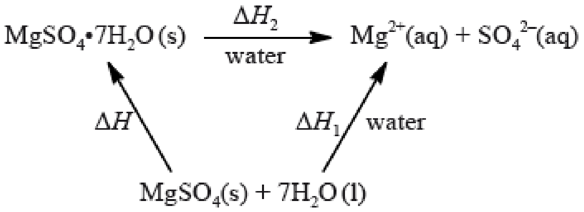
c.iii. 1.00 mol of CH_3OH is placed in a closed container of volume $1.00\ \text{dm}^3$ until equilibrium is reached with CO and H_2. At equilibrium 0.492 mol of CH_3OH are present. Calculate K_c. [3]

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, $\text{MgSO}_4(\text{s})$, was dissolved in water. They presented their results in the table below.

mass of anhydrous magnesium sulfate / g	3.01
volume of water / 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, $\text{MgSO}_4 \bullet 7\text{H}_2\text{O(s)}$, and $50.0\ \text{cm}^3$ of water. They found the enthalpy change, ΔH_2 , to be $+18\ \text{kJ mol}^{-1}$.

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 kJ mol^{-1}. State your answer to the correct number of significant figures.

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

(ii) The literature value for the enthalpy of hydration of anhydrous magnesium sulfate is $-103\ \text{kJ mol}^{-1}$. 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 $-100\ \text{kJ mol}^{-1}$, but this is **not** the correct value.)

c. Another group of students experimentally determined an enthalpy of hydration of $-95\ \text{kJ mol}^{-1}$. 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.

One important property of a rocket fuel mixture is the large volume of gaseous products formed which provide thrust. Hydrazine, N_2H_4, is often used as a rocket fuel. The combustion of hydrazine is represented by the equation below.

$$\mathrm{N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)} \quad \Delta H_c^{\ominus} = -585\ \text{kJ mol}^{-1}$$

Comment on the environmental safety of the products of the reaction of N_2H_4 with O_2 **and** the reaction of N_2H_4 with F_2.

Hydrazine, N_2H_4, is a valuable rocket fuel.

The equation for the reaction between hydrazine and oxygen is given below.

$$\mathrm{N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)}$$

The reaction between $N_2H_4(aq)$ and $HCl(aq)$ can be represented by the following equation.

$$N_2H_4(aq) + 2HCl(aq) \rightarrow N_2H_6^{2+}(aq) + 2Cl^-(aq)$$

a. (i) Draw the Lewis (electron dot) structure for N_2H_4 showing all valence electrons. [4]

(ii) State and explain the H–N–H bond angle in hydrazine.

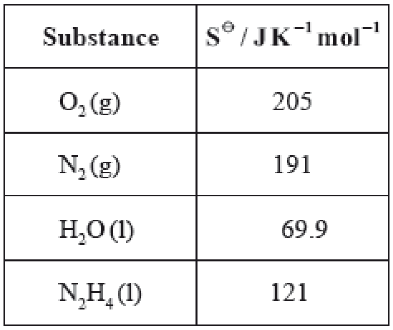
b. Hydrazine and ethene, C_2H_4, are hydrides of adjacent elements in the periodic table. The boiling point of hydrazine is much higher than that of ethene. Explain this difference in terms of the intermolecular forces in each compound. [2]

c. (i) The enthalpy change of formation, ΔH_f^Θ, of liquid hydrazine is $50.6\ \text{kJ mol}^{-1}$. Use this value, together with data from Table 12 of the Data Booklet, to calculate the enthalpy change for this reaction. [16]

(ii) Use the bond enthalpy values from Table 10 of the Data Booklet to determine the enthalpy change for this reaction.

(iii) Identify the calculation that produces the most accurate value for the enthalpy change for the reaction given and explain your choice.

(iv) Calculate ΔS^Θ for the reaction using the data below and comment on its magnitude.



Substance	$S^\Theta / J K^{-1} mol^{-1}$
$O_2(g)$	205
$N_2(g)$	191
$H_2O(l)$	69.9
$N_2H_4(l)$	121

(v) Calculate ΔG^Θ for the reaction at 298 K.

(vi) Predict, giving a reason, the spontaneity of the reaction above at both high and low temperatures.

d. The reaction between $N_2H_4(aq)$ and HCl(aq) can be represented by the following equation. [3]

$$N_2H_4(aq) + 2HCl(aq) \rightarrow N_2H_6^{2+}(aq) + 2Cl^-(aq)$$

(i) Identify the type of reaction that occurs.

(ii) Predict the value of the H–N–H bond angle in $N_2H_6^{2+}$.

(iii) Suggest the type of hybridization shown by the nitrogen atoms in $N_2H_6^{2+}$.

Phosphoryl chloride, $POCl_3$, is a dehydrating agent.

$POCl_3$ (g) decomposes according to the following equation.

$$2POCl_3(g) \rightarrow 2PCl_3(g) + O_2(g)$$

$POCl_3$ can be prepared by the reaction of phosphorus pentachloride, PCl_5 , with tetraphosphorus decaoxide, P_4O_{10}.

PCl_3 and Cl^- can act as ligands in transition metal complexes such as $Ni(PCl_3)_4$ and $[Cr(H_2O)_3Cl_3]$.

a.i. Predict and explain the sign of the entropy change, ΔS, for this reaction. [1]

a.ii.Calculate the standard entropy change for the reaction, ΔS^{Θ}, in $\mathrm{J\,K^{-1} mol^{-1}}$, using the data below. [1]

Substance	S^{Θ} / J K^{-1} mol^{-1}
$POCl_3$ (g)	325.0
PCl_3 (g)	311.7
O_2 (g)	205.0

a.iiiDefine the term *standard enthalpy change of formation*, ΔH_f^{Θ}. [1]

a.ivCalculate the standard enthalpy change for the reaction, ΔH^{Θ}, in $\mathrm{kJ\,mol^{-1}}$, using the data below. [1]

Substance	ΔH_f^{Θ} / kJ mol^{-1}
$POCl_3$ (g)	–542.2
PCl_3 (g)	–288.1

a.v.Determine the standard free energy change for the reaction, ΔG^{Θ}, in $\mathrm{kJ\,mol^{-1}}$, at 298 K. [1]

a.viDeduce the temperature, in K, at which the reaction becomes spontaneous. [1]

b.i.Deduce the Lewis (electron dot) structure of $POCl_3$ (with P as the central element) and PCl_3 and predict the shape of each molecule, using the valence shell electron pair repulsion theory (VSEPR). [4]

b.ii.State and explain the Cl–P–Cl bond angle in PCl_3. [3]

c.i.Deduce the Lewis (electron dot) structure of PCl_5. [1]

c.ii.Predict the shape of this molecule, using the valence shell electron pair repulsion theory (VSEPR). [1]

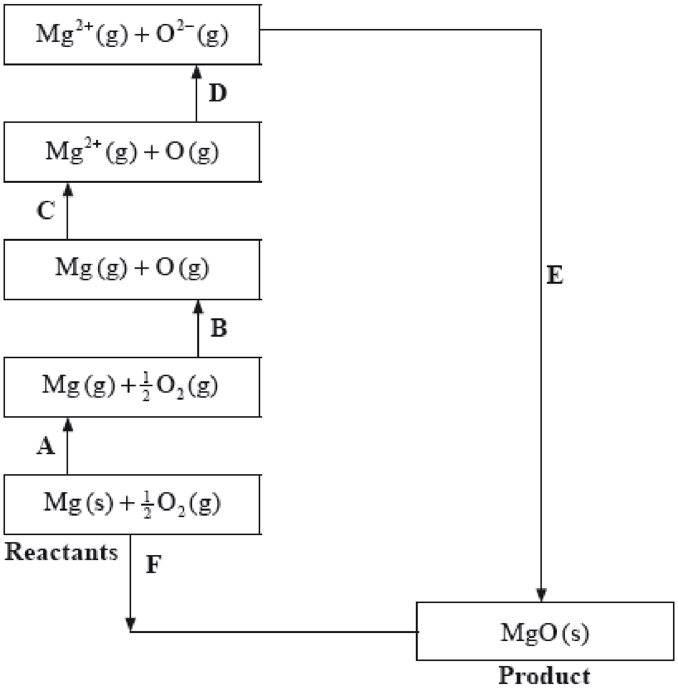
c.iiiIdentify all the different bond angles in PCl_5. [1]

c.ivPCl$_3$Br$_2$ has the same molecular shape as PCl_5. Draw the three isomers of PCl_3Br_2 and deduce whether each isomer is polar or non-polar. [3]

d.i.Define the term *ligand*. [2]

d.ii.Explain why the complex $[Cr(H_2O)_3Cl_3]$ is coloured. [3]

The Born-Haber cycle for MgO under standard conditions is shown below.



The values are shown in the table below.

Process	Enthalpy change / kJ mol^{-1}
A	+150
B	+248
C	+736 + (+1450)
D	−142 + (+844)
E	
F	−602

a.i. Identify the processes represented by **A**, **B** and **D** in the cycle. [3]

a.ii. Define the enthalpy change, **F**. [2]

a.iii. Determine the value of the enthalpy change, **E**. [2]

a.iv. Define the enthalpy change **C** for the first value. Explain why the second value is significantly larger than the first. [4]

a.v. The inter-ionic distance between the ions in NaF is very similar to that between the ions in MgO. Suggest with a reason, which compound has the higher lattice enthalpy value. [2]

b.i. The standard enthalpy change of three combustion reactions is given below in kJ. [4]

$$\begin{array}{ll} 2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) & \Delta H^\Theta = -3120 \\ 2H_2(g) + O_2(g) \rightarrow 2H_2O(l) & \Delta H^\Theta = -572 \\ C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) & \Delta H^\Theta = -1411 \end{array}$$

Based on the above information, calculate the standard change in enthalpy, ΔH^Θ, for the following reaction.

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

b.ii. Predict, stating a reason, whether the sign of ΔS^Θ for the above reaction would be positive or negative. [2]

b.iii. Discuss why the above reaction is non-spontaneous at low temperature but becomes spontaneous at high temperatures. [2]

b.iv. Using bond enthalpy values, calculate $\Delta H^{\ominus}$ for the following reaction. [3]

$$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$$

b.v. Suggest with a reason, why the values obtained in parts (b) (i) and (b) (iv) are different. [1]

Two students were asked to use information from the Data Booklet to calculate a value for the enthalpy of hydrogenation of ethene to form ethane.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

John used the average bond enthalpies from Table 10. Marit used the values of enthalpies of combustion from Table 12.

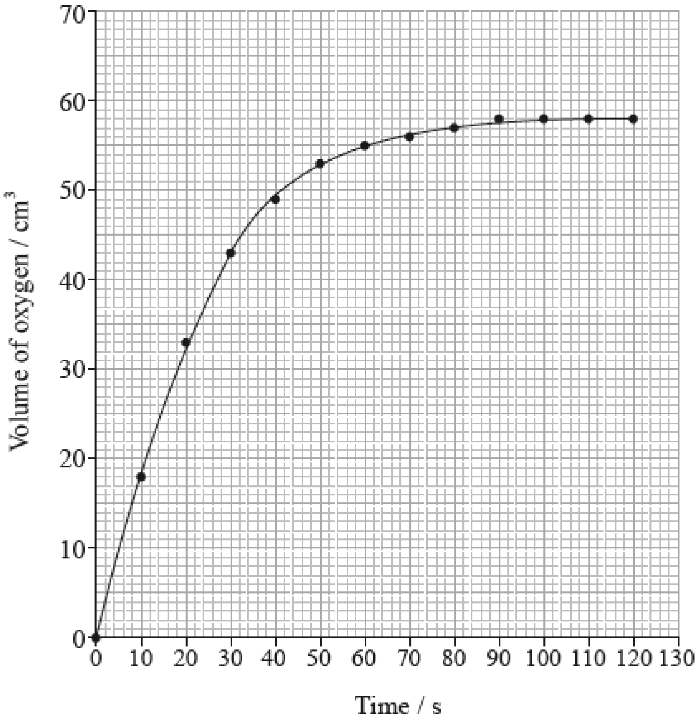
b. Determine the value for the enthalpy of hydrogenation of ethene using the values for the enthalpies of combustion of ethene, hydrogen and ethane given in Table 12. [2]

c. Suggest **one** reason why John's answer is slightly less accurate than Marit's answer and calculate the percentage difference. [2]

Hydrogen peroxide decomposes according to the equation below.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

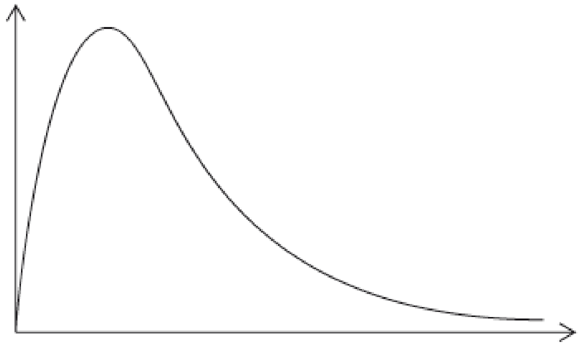
The rate of the decomposition can be monitored by measuring the volume of oxygen gas released. The graph shows the results obtained when a solution of hydrogen peroxide decomposed in the presence of a CuO catalyst.



a.i. Outline how the initial rate of reaction can be found from the graph. [2]

a.ii. Explain how and why the rate of reaction changes with time. [3]

b. A Maxwell-Boltzmann energy distribution curve is drawn below. Label both axes and explain, by annotating the graph, how catalysts increase the rate of reaction. [3]



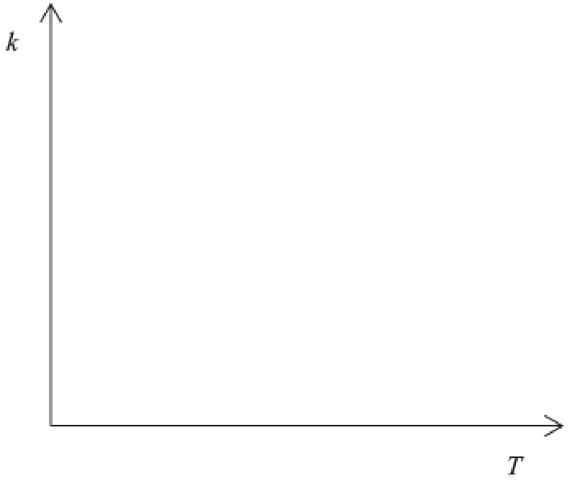
c. (i) In some reactions, increasing the concentration of a reactant does not increase the rate of reaction. Describe how this may occur. [2]

(ii) Consider the reaction

$$2A + B \rightarrow C + D$$

The reaction is first order with respect to **A**, and zero order with respect to **B**. Deduce the rate expression for this reaction.

d. Sketch a graph of rate constant (k) versus temperature. [1]



e. Hydrochloric acid neutralizes sodium hydroxide, forming sodium chloride and water. [9]

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) \quad \Delta H^\ominus = -57.9\ kJ\ mol^{-1}$$

(i) Define *standard enthalpy change of reaction*, $\Delta H^\ominus$.

(ii) Determine the amount of energy released, in kJ, when $50.0\ cm^3$ of $1.00\ mol\ dm^{-3}$ sodium hydroxide solution reacts with $50.0\ cm^3$ of $1.00\ mol\ dm^{-3}$ hydrochloric acid solution.

(iii) In an experiment, 2.50 g of solid sodium hydroxide was dissolved in $50.0\ cm^3$ of water. The temperature rose by 13.3 °C. Calculate the standard enthalpy change, in $kJ\ mol^{-1}$, for dissolving one mole of solid sodium hydroxide in water.

$$NaOH(s) \rightarrow NaOH(aq)$$

(iv) Using relevant data from previous question parts, determine $\Delta H^\ominus$, in $kJ\ mol^{-1}$, for the reaction of solid sodium hydroxide with hydrochloric acid.

$$NaOH(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

f. (i) Zinc is found in the d-block of the periodic table. Explain why it is not considered a transition metal. [5]

(ii) Explain why Fe^{3+} is a more stable ion than Fe^{2+} by reference to their electron configurations.

Consider the following reaction.

$$2\mathrm{CH_3OH(g)} + \mathrm{H_2(g)} \rightarrow \mathrm{C_2H_6(g)} + 2\mathrm{H_2O(g)}$$

a. The standard enthalpy change of formation for $\mathrm{CH_3OH(g)}$ at 298 K is $-201\ \mathrm{kJ\,mol^{-1}}$ and for $\mathrm{H_2O(g)}$ is $-242\ \mathrm{kJ\,mol^{-1}}$. Using information from Table 11 of the Data Booklet, determine the enthalpy change for this reaction. [2]

b. The standard entropy for $\mathrm{CH_3OH(g)}$ at 298 K is $238\ \mathrm{J\,K^{-1}mol^{-1}}$, for $\mathrm{H_2(g)}$ is $131\ \mathrm{J\,K^{-1}mol^{-1}}$ and for $\mathrm{H_2O(g)}$ is $189\ \mathrm{J\,K^{-1}mol^{-1}}$. Using information from Table 11 of the Data Booklet, determine the entropy change for this reaction. [2]

c. Calculate the standard change in free energy, at 298 K, for the reaction and deduce whether the reaction is spontaneous or non-spontaneous. [3]

Ethanol has many industrial uses.

a. State an equation for the formation of ethanol from ethene and the necessary reaction conditions. [3]

Equation:

Conditions:

b.i. Define the term *average bond enthalpy*. [2]

b.ii. Ethanol can be used as a fuel. Determine the enthalpy of combustion of ethanol at 298 K, in $\mathrm{kJ\,mol^{-1}}$, using the values in table 10 of the data booklet, assuming all reactants and products are gaseous. [4]

c. Students can also measure the enthalpy of combustion of ethanol in the laboratory using calorimetry. Suggest the major source of systematic error in these procedures. [1]

d. State the equation for the acid-catalysed reaction of ethanol with propanoic acid and state the name of the organic product. [2]

Equation:

Name of the organic product:

e.i. A polyester can be formed when ethane-1,2-diol reacts with benzene-1,4-dicarboxylic acid. [2]

Deduce the structure of the repeating unit and state the other product formed.

Repeating unit:

Other product:

e.ii. State the type of polymerization that occurs. [1]

f.i. The standard enthalpy change of combustion, $\Delta H_c^\ominus$, of propanoic acid is $-1527\ \mathrm{kJ\ mol^{-1}}$. Determine the standard enthalpy change of formation of propanoic acid, in $\mathrm{kJ\ mol^{-1}}$, using this information and data from table 12 of the data booklet. [4]

f.ii. Deduce, giving a reason, the sign of the standard entropy change of the system for the formation of propanoic acid from its elements. [2]

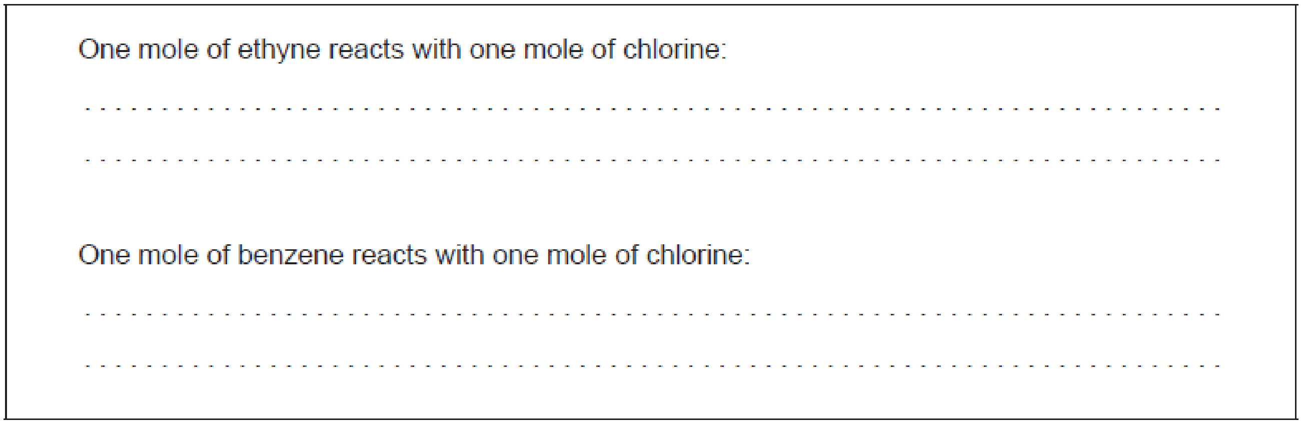
g. Identify **three** allotropes of carbon and describe their structures. [4]

This question is about ethene, C_2H_4, and ethyne, C_2H_2.

a.i. Ethyne, like ethene, undergoes hydrogenation to form ethane. State the conditions required. [2]

a.ii. Outline the formation of polyethene from ethene by drawing three repeating units of the polymer. [1]

b. Ethyne reacts with chlorine in a similar way to ethene. Formulate equations for the following reactions. [2]



One mole of ethyne reacts with one mole of chlorine:

. . . .

. . . .

One mole of benzene reacts with one mole of chlorine:

. . . .

. . . .

c.i. Under certain conditions, ethyne can be converted to benzene. [2]

Determine the standard enthalpy change, $\Delta H^\ominus$, for the reaction stated, using section 11 of the data booklet.

$$3C_2H_2(g) \rightarrow C_6H_6(g)$$

c.ii. Determine the standard enthalpy change, $\Delta H^\ominus$, for the following similar reaction, using ΔH_f values in section 12 of the data booklet. [2]

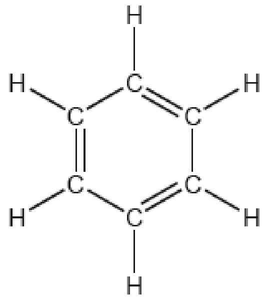
$$3C_2H_2(g) \rightarrow C_6H_6(l)$$

c.iii Explain, giving two reasons, the difference in the values for (c)(i) and (ii). If you did not obtain answers, use −475 kJ for (i) and −600 kJ for (ii). [2]

c.iv Calculate the standard entropy change, $\Delta S^\ominus$, in $\mathrm{J\ K^{-1}}$, for the reaction in (ii) using section 12 of the data booklet. [1]

c.v. Determine, showing your working, the spontaneity of the reaction in (ii) at 25 °C. [3]

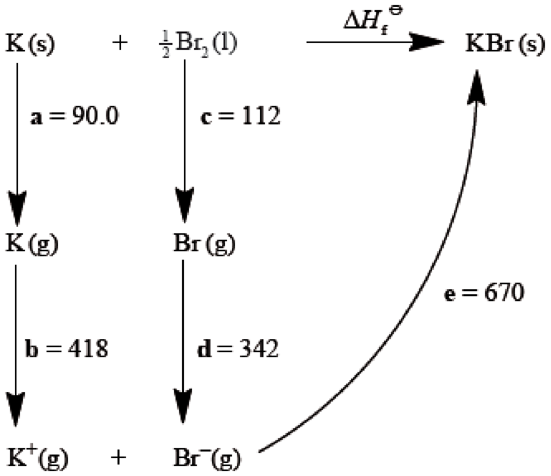
d. One possible Lewis structure for benzene is shown. [1]



State one piece of physical evidence that this structure is **incorrect**.

Draw the Lewis structures, state the shape and predict the bond angles for the following species.

Consider the following Born-Haber cycle:



The magnitudes for each of the enthalpy changes (**a** to **e**) are given in kJ mol^{-1} but their signs (+ or −) have been omitted.

a.i. PCl_3 [3]

a.ii. NH_2^- [3]

a.iii. XeF_4 [3]

b.i. State the names for the enthalpy changes **c** and **d**. [2]

b.ii. Deduce which **two** of the enthalpy changes **a** to **e** have negative signs. [1]

b.iii. Determine the value for the enthalpy of formation of potassium bromide. [2]

b.iv. Explain why the quantitative value for the lattice enthalpy of calcium bromide is larger than the value for the lattice enthalpy of potassium bromide. [2]

c.i. Compare the formation of a sigma (σ) and a pi (π) bond between two carbon atoms in a molecule. [2]

c.ii.Identify how many sigma and pi bonds are present in propene, C_3H_6. [2]

c.iiiDeduce all the bond angles present in propene. [2]

c.ivExplain how the concept of hybridization can be used to explain the bonding in the triple bond present in propyne. [3]

Carbon monoxide reacts with hydrogen to produce methanol.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

Substance	$\Delta H_f^\ominus$ / kJ mol^{-1}	$\Delta G_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J mol^{-1} K^{-1}
CO (g)	– 110.5	– 137.2	+ 197.6
CH_3OH (l)	– 239.0	– 166.0	+ 126.8

a. Calculate the standard enthalpy change, ΔH^Θ, in $\mathrm{kJ\,mol^{-1}}$, for the reaction. [1]

b. Calculate the standard free energy change, ΔG^Θ, in $\mathrm{kJ\,mol^{-1}}$, for the reaction [1]

$(\Delta G_f^\Theta(H_2) = 0\ \mathrm{kJ\,mol^{-1}})$.

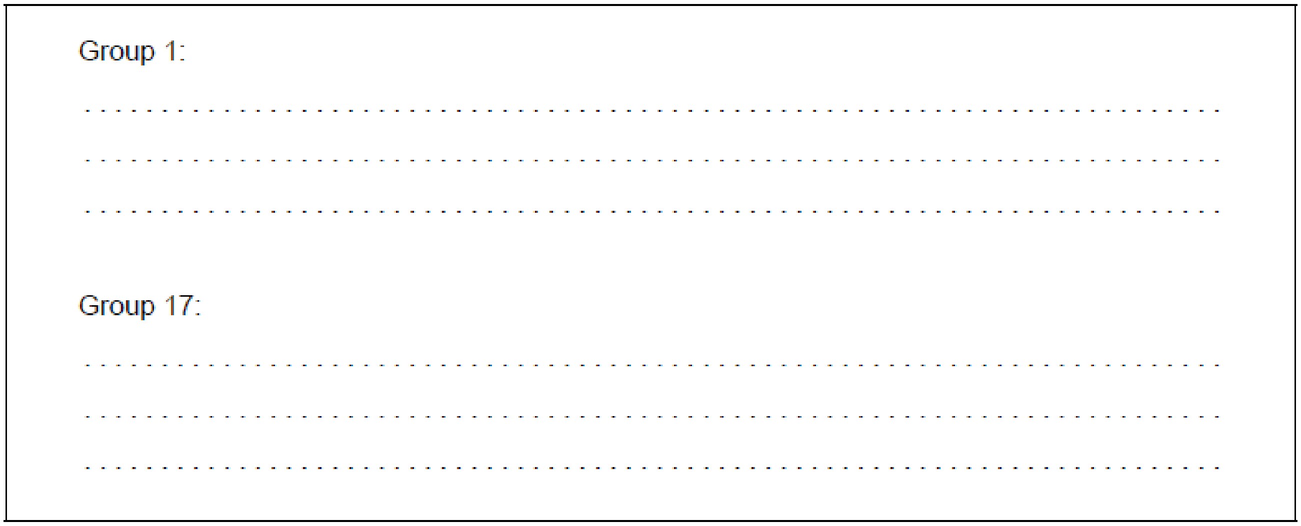
c. Using the values obtained in parts (a) and (b), calculate the standard entropy change, ΔS^Θ, in $\mathrm{J\ mol^{-1}K^{-1}}$, for the reaction at 298 K. [1]

d. Determine the absolute entropy, S^Θ, in $\mathrm{J\,mol^{-1}K^{-1}}$, for $H_2(g)$ at 298 K. [2]

Trends in physical and chemical properties are useful to chemists.

Cobalt forms the transition metal complex $[Co(NH_3)_4(H_2O)Cl]Br$.

b. Explain why the melting points of the group 1 metals (Li → Cs) decrease down the group whereas the melting points of the group 17 elements (F → I) increase down the group. [3]



Group 1:

. . . .

. . . .

. . . .

Group 17:

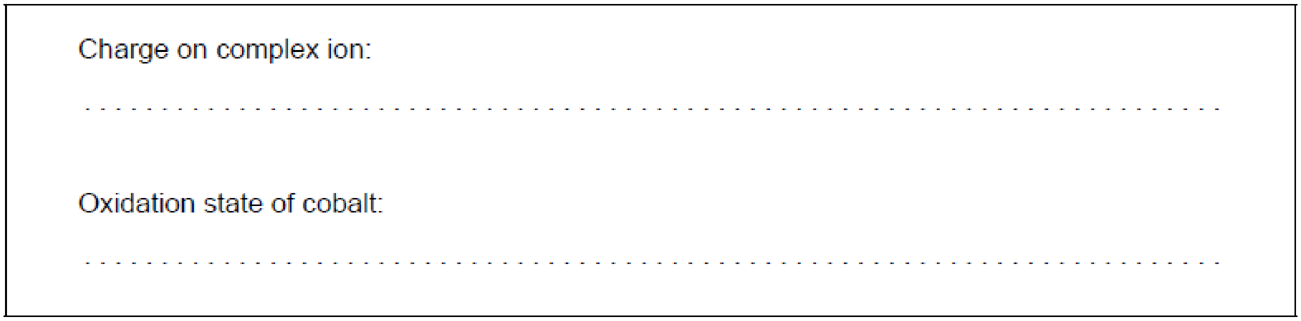
. . . .

. . . .

. . . .

d.i. State the shape of the complex ion. [1]

d.ii. Deduce the charge on the complex ion and the oxidation state of cobalt. [2]



Charge on complex ion:

. . . .

Oxidation state of cobalt:

. . . .

e. Describe, in terms of acid-base theories, the type of reaction that takes place between the cobalt ion and water to form the complex ion. [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, N_2. [2]

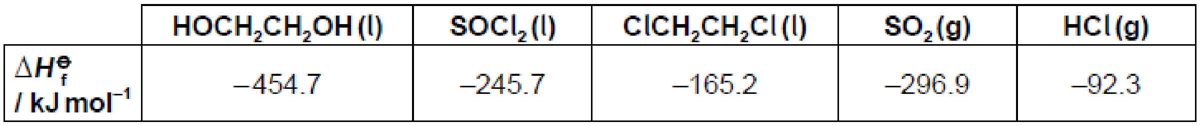
h. Deduce the N–N–N bond angle in trinitramide and explain your reasoning. [3]

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

Ethane-1,2-diol, $HOCH_2CH_2OH$, reacts with thionyl chloride, $SOCl_2$, according to the reaction below.

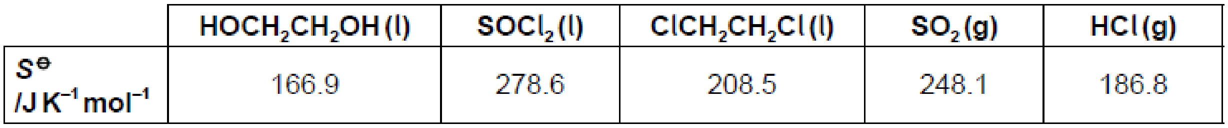
$$HOCH_2CH_2OH\,(l) + 2SOCl_2\,(l) \rightarrow ClCH_2CH_2Cl\,(l) + 2SO_2\,(g) + 2HCl\,(g)$$

a. Calculate the standard enthalpy change for this reaction using the following data. [2]



	$HOCH_2CH_2OH\,(l)$	$SOCl_2\,(l)$	$ClCH_2CH_2Cl\,(l)$	$SO_2\,(g)$	$HCl\,(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−454.7	−245.7	−165.2	−296.9	−92.3

b. Calculate the standard entropy change for this reaction using the following data. [1]



	$HOCH_2CH_2OH\,(l)$	$SOCl_2\,(l)$	$ClCH_2CH_2Cl\,(l)$	$SO_2\,(g)$	$HCl\,(g)$
$S^{\ominus}$ /J K^{-1} mol^{-1}	166.9	278.6	208.5	248.1	186.8

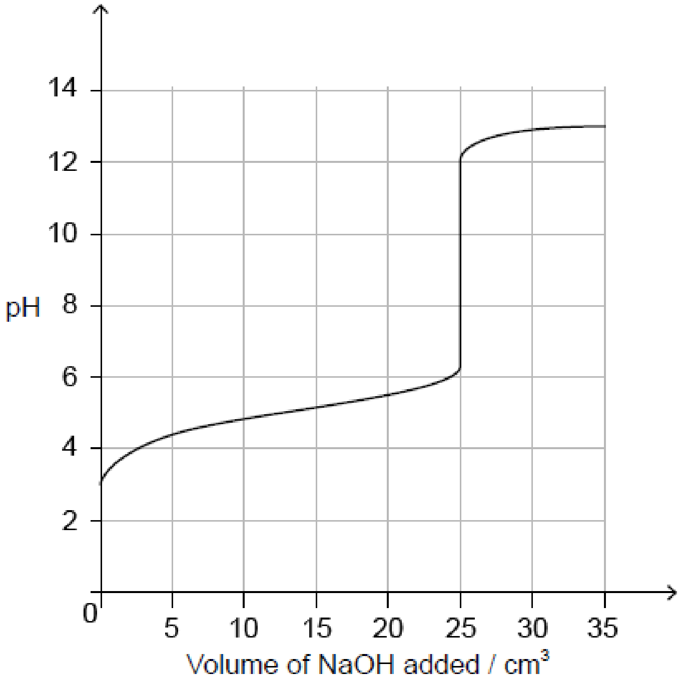
c. The standard free energy change, ΔG^{θ}, for the above reaction is –103 kJ mol^{-1} at 298 K. [2]

Suggest why ΔG^{θ} has a large negative value considering the sign of ΔH^{θ} in part (a).

Soluble acids and bases ionize in water.

A solution containing 0.510 g of an unknown monoprotic acid, HA, was titrated with 0.100 mol dm^{-3} NaOH(aq). 25.0 cm^{3} was required to reach the equivalence point.

b.iv The following curve was obtained using a pH probe. [1]



State, giving a reason, the strength of the acid.

b.v. State a technique other than a pH titration that can be used to detect the equivalence point. [1]

b.vi. Deduce the pK_a for this acid. [1]

c. The pK_a of an anthocyanin is 4.35. Determine the pH of a 1.60×10^{-3} mol dm^{-3} solution to two decimal places. [3]

Ethane-1,2-diol, $HOCH_2CH_2OH$, has a wide variety of uses including the removal of ice from aircraft and heat transfer in a solar cell.

b. (i) Calculate ΔH^θ, in kJ, for this similar reaction below using ΔH_f^θ data from section 12 of the data booklet. ΔH_f^θ of $HOCH_2CH_2OH(l)$ is –454.8kJmol^{-1}. [6]

$$2CO\ (g) + 3H_2\ (g) \rightleftharpoons HOCH_2CH_2OH\ (l)$$

(ii) Deduce why the answers to (a)(iii) and (b)(i) differ.

(iii) ΔS^θ for the reaction in (b)(i) is –620.1JK^{-1}. Comment on the decrease in entropy.

(iv) Calculate the value of ΔG^θ, in kJ, for this reaction at 298 K using your answer to (b)(i). (If you did not obtain an answer to (b)(i), use –244.0 kJ, but this is not the correct value.)

(v) Comment on the statement that the reaction becomes less spontaneous as temperature is increased.

f. Predict the ^{1}HNMR data for ethanedioic acid and ethane-1,2-diol by completing the table. [2]

	Number of signals	**Splitting pattern**
Ethanedioic acid:	. . . .	. . . .
Ethane-1,2-diol:	. . . .	Not required

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, $\Delta H_c^\ominus = -750\,\text{kJ}\,\text{mol}^{-1}$

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

(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:

The reaction between hydrogen and nitrogen monoxide is thought to proceed by the mechanism shown below.

$$2\text{NO}(g) \rightleftharpoons \text{N}_2\text{O}_2(g) \qquad \text{fast equilibrium}$$

$$\text{N}_2\text{O}_2(g) + \text{H}_2(g) \rightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g) \qquad \text{slow reaction}$$

$$\text{N}_2\text{O}(g) + \text{H}_2(g) \rightarrow \text{N}_2(g) + \text{H}_2\text{O}(g) \qquad \text{fast reaction}$$

a. (i) State the equation for the overall reaction. [7]

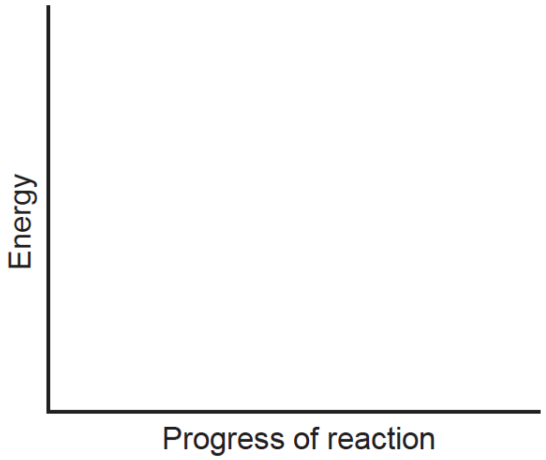
(ii) Deduce the rate expression consistent with this mechanism.

(iii) Explain how you would attempt to confirm this rate expression, giving the results you would expect.

(iv) State, giving your reason, whether confirmation of the rate expression would prove that the mechanism given is correct.

(v) Suggest how the rate of this reaction could be measured experimentally.

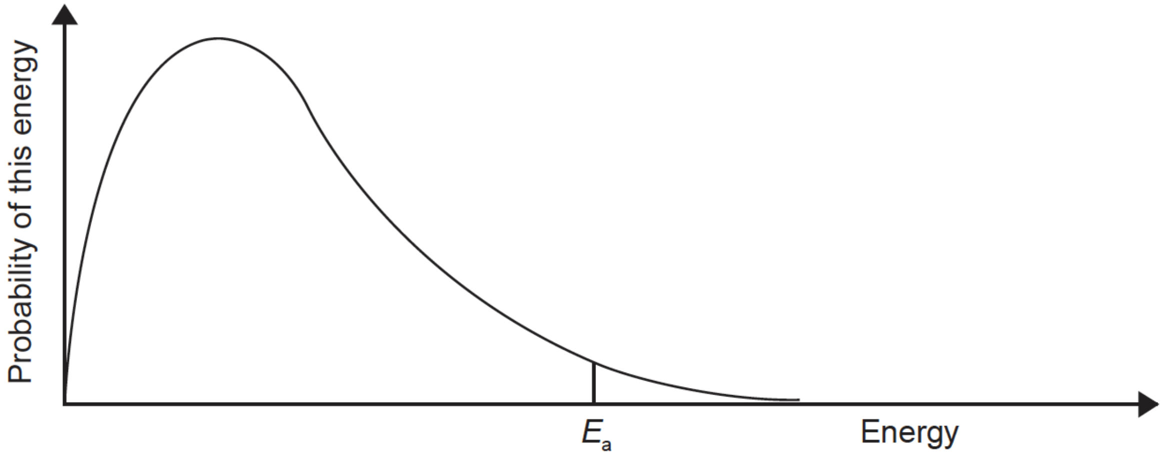
b. The enthalpy change for the reaction between nitrogen monoxide and hydrogen is –664 kJ and its activation energy is 63 kJ. [6]



(i) Sketch the potential energy profile for the overall reaction, using the axes given, indicating both the enthalpy of reaction and activation energy.

(ii) This reaction is normally carried out using a catalyst. Draw a dotted line labelled "Catalysed" on the diagram above to indicate the effect of the catalyst.

(iii) Sketch and label a second Maxwell–Boltzmann energy distribution curve representing the same system but at a higher temperature, T_{higher}.



(iv) Explain why an increase in temperature increases the rate of this reaction.

c. One of the intermediates in the reaction between nitrogen monoxide and hydrogen is dinitrogen monoxide, N_2O. This can be represented by the resonance structures below: [4]

(i) Analyse the bonding in dinitrogen monoxide in terms of σ-bonds and Δ-bonds.

(ii) State what is meant by resonance.

Phosgene, $COCl_2$, is usually produced by the reaction between carbon monoxide and chlorine according to the equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

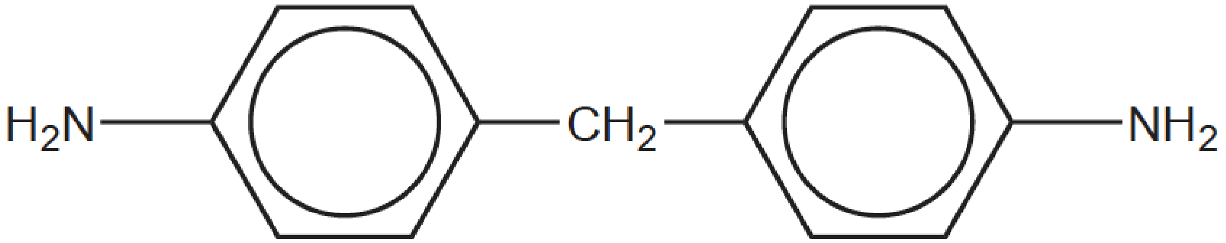
a. (i) Deduce the equilibrium constant expression, K_c, for this reaction. [8]

(ii) At exactly 600°C the value of the equilibrium constant is 0.200. Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the reaction, in kJ, using sections 1 and 2 of the data booklet. State your answer to **three** significant figures.

(iii) The standard enthalpy change of formation of phosgene, $\Delta H_f^{\ominus}$, is -220.1kJmol^{-1}. Determine the standard enthalpy change, $\Delta H^{\ominus}$, for the forward reaction of the equilibrium, in kJ, using section 12 of the data booklet.

(iv) Calculate the standard entropy change, $\Delta S^{\ominus}$, in JK^{-1}, for the forward reaction at 25°C, using your answers to (a) (ii) and (a) (iii). (If you did not obtain an answer to (a) (ii) and/or (a) (iii) use values of +20.0 kJ and −120.0 kJ respectively, although these are not the correct answers.)

b. One important industrial use of phosgene is the production of polyurethanes. Phosgene is reacted with diamine **X**, derived from phenylamine. [8]



X

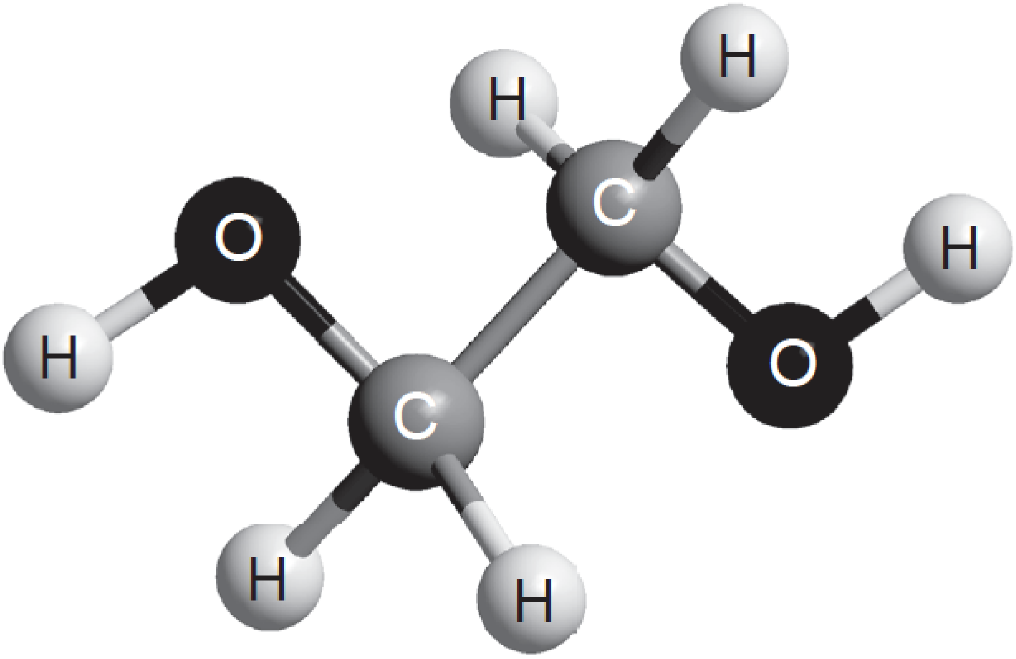
(i) Classify diamine **X** as a primary, secondary or tertiary amine.

(ii) Phenylamine, $C_6H_5NH_2$, is produced by the reduction of nitrobenzene, $C_6H_5NO_2$. Suggest how this conversion can be carried out.

(iii) Nitrobenzene can be obtained by nitrating benzene using a mixture of concentrated nitric and sulfuric acids. Formulate the equation for the equilibrium established when these two acids are mixed.

(iv) Deduce the mechanism for the nitration of benzene, using curly arrows to indicate the movement of electron pairs.

c. The other monomer used in the production of polyurethane is compound **Z** shown below. [5]



(i) State the name, applying IUPAC rules, of compound **Z** and the class of compounds to which it belongs.

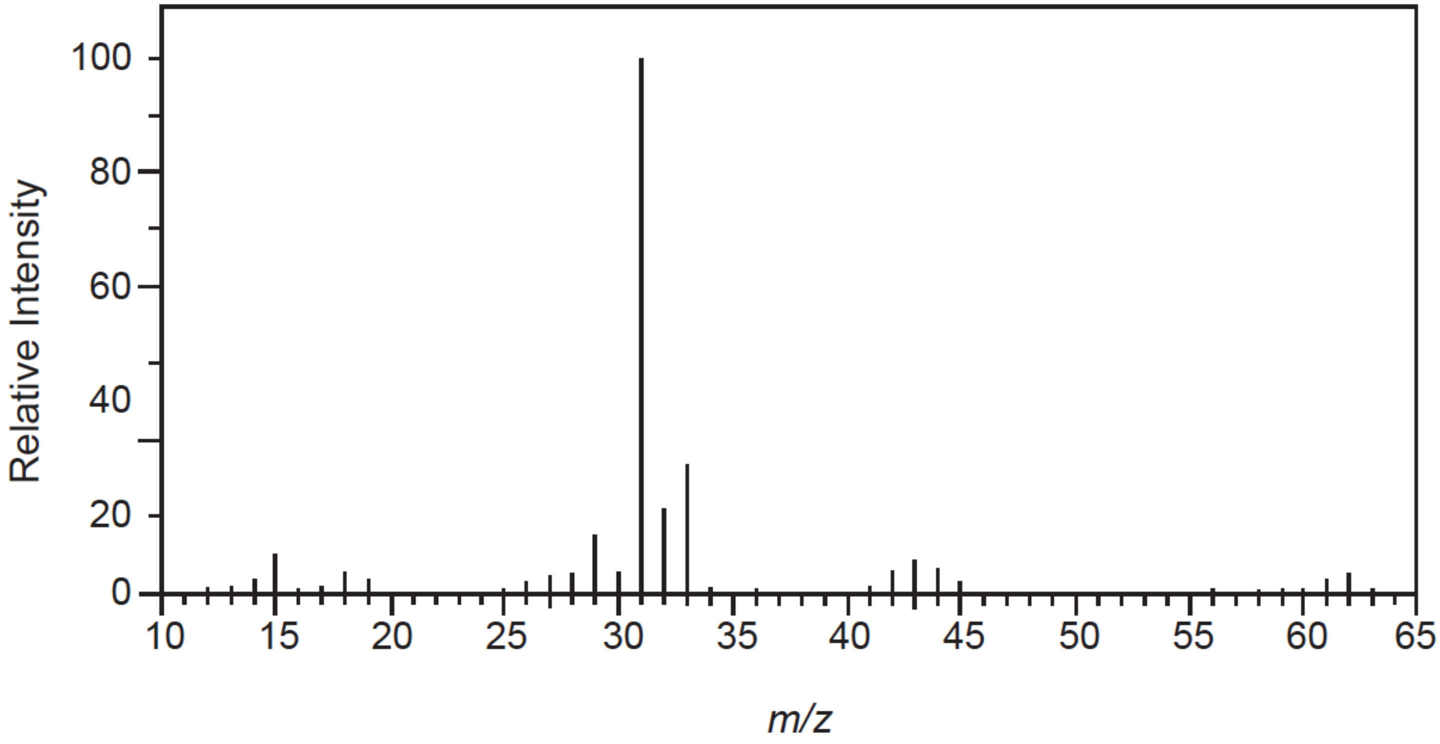
Name:

Class:

(ii) Deduce the number of signals you would expect to find in the ^{1}H NMR spectrum of compound **Z**, giving your reasons.

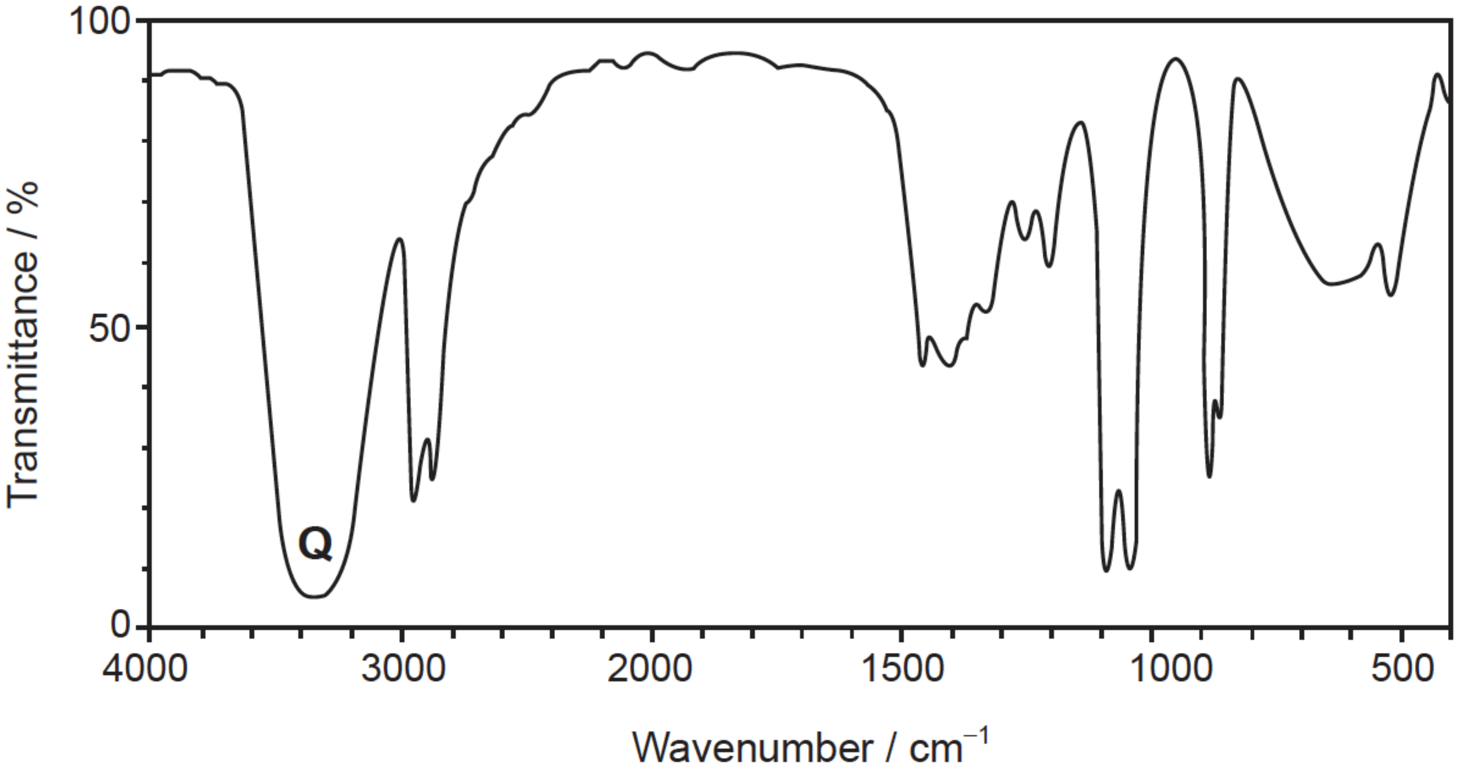
The mass spectrum and infrared (IR) spectrum of compound **Z** are shown below:

Mass spectrum



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

IR spectrum



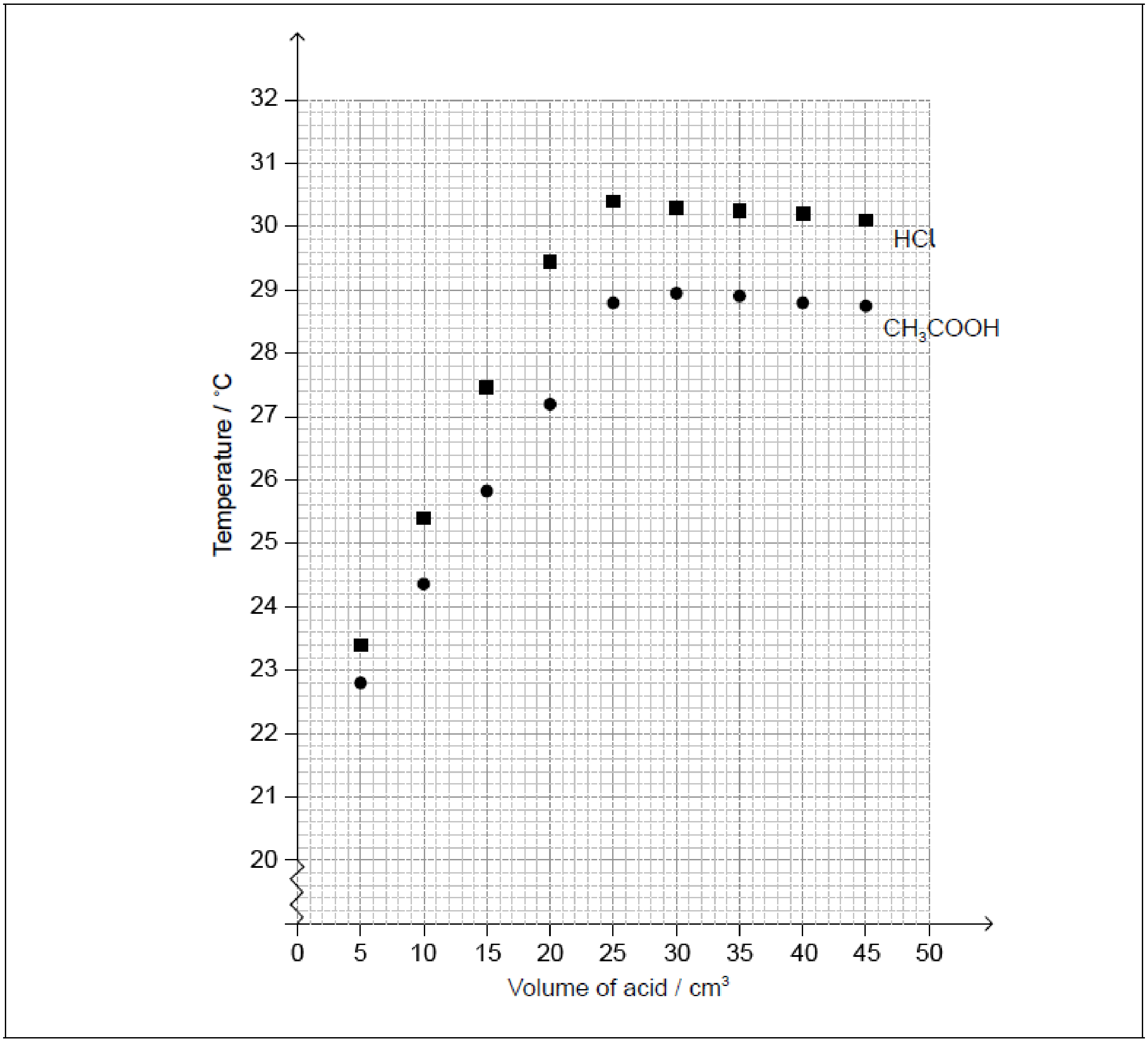
[Source: http://sdbs.db.aist.go.jp]

(iii) Identify the species causing the large peak at *m*/*z*=31 in the mass spectrum.

(iv) Identify the bond that produces the peak labelled **Q** on the IR spectrum, using section 26 of the data booklet.

d. Phenylamine can act as a weak base. Calculate the pH of a 0.0100 mol dm^{-3} solution of phenylamine at 298K using section 21 of the data booklet. [4]

A student titrated two acids, hydrochloric acid, HCl (aq) and ethanoic acid, CH_3COOH (aq), against 50.0 cm^3 of 0.995 mol dm^{-3} sodium hydroxide, NaOH (aq), to determine their concentration. The temperature of the reaction mixture was measured after each acid addition and plotted against the volume of each acid.



a. Using the graph, estimate the initial temperature of the solutions. [1]

b. Determine the maximum temperature reached in each experiment by analysing the graph. [2]

HCl:

. . . .

CH_3COOH:

. . . .

e. Suggest why the enthalpy change of neutralization of CH_3COOH is less negative than that of HCl. [2]