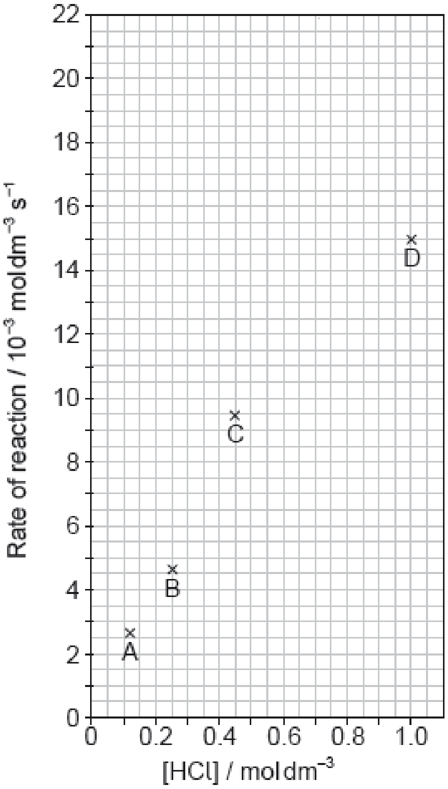
HL Paper 2

Calcium carbonate reacts with hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The results of a series of experiments in which the concentration of HCl was varied are shown below.



a. Outline **two** ways in which the progress of the reaction can be monitored. No practical details are required. [2]

b.i. Suggest why point D is so far out of line assuming human error is not the cause. [1]

b.ii. Draw the best fit line for the reaction excluding point D. [1]

b.iii. Suggest the relationship that points A, B and C show between the concentration of the acid and the rate of reaction. [1]

b.iv. Deduce the rate expression for the reaction. [1]

b.v. Calculate the rate constant of the reaction, stating its units. [2]

c. Predict from your line of best fit the rate of reaction when the concentration of HCl is 1.00 mol dm^{-3}. [1]

d. Describe how the activation energy of this reaction could be determined. [3]

Markscheme

a. *Any two of:*

loss of mass «of reaction mixture/CO_2»

«increase in» volume of gas produced

change of conductivity

change of pH

change in temperature

*Do **not** accept "disappearance of calcium carbonate".*

*Do **not** accept "gas bubbles".*

*Do **not** accept "colour change" or "indicator".*

[2 marks]

b.i. reaction is fast at high concentration ***AND*** may be difficult to measure accurately

OR

so many bubbles of CO_2 produced that inhibit contact of HCl(aq) with $CaCO_3$(s)

OR

insufficient change in conductivity/pH at high concentrations

OR

calcium carbonate has been used up/is limiting reagent/ there is not enough calcium carbonate «to react with the high concentration of HCl»

OR

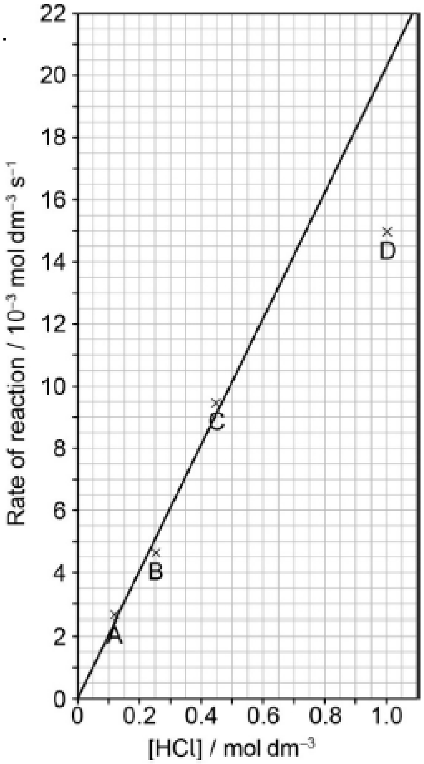
HCl is in excess

OR

so many bubbles of CO_2 produced that inhibit contact of HCl(aq) with $CaCO_3$(s)

[1 mark]

b.ii.



straight line going through the origin ***AND*** as close to A, B, C as is reasonably possible

[1 mark]

b.iii. «directly» proportional

Accept "first order" or "linear".

Do ***not*** *accept "rate increases as concentration increases" or "positive correlation".*

[1 mark]

b.iv. rate = k [H^+]

Accept "rate = k [HCl]".

[1 mark]

b.v. 0.02

s^{-1}

[2 marks]

c. 20.5×10^{-3} «mol dm^{-3} s^{-1}»

Accept any answer in the range 19.5–21.5.

[1 mark]

d. ***ALTERNATIVE 1:***

carry out reaction at several temperatures

plot $\frac{1}{T}$ against log rate constant

E_a = – gradient × R

ALTERNATIVE 2:

carry out reaction at two temperatures

determine two rate constants

OR

determine the temperature coefficient of the rate

use the formula $\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Accept "gradient = $\frac{-E_a}{R}$*" for M3.*

Award both M2 and M3 for the formula $\ln\frac{rate_1}{rate_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$.

Accept any variation of the formula, such as $\frac{rate_1}{rate_2} = e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$.

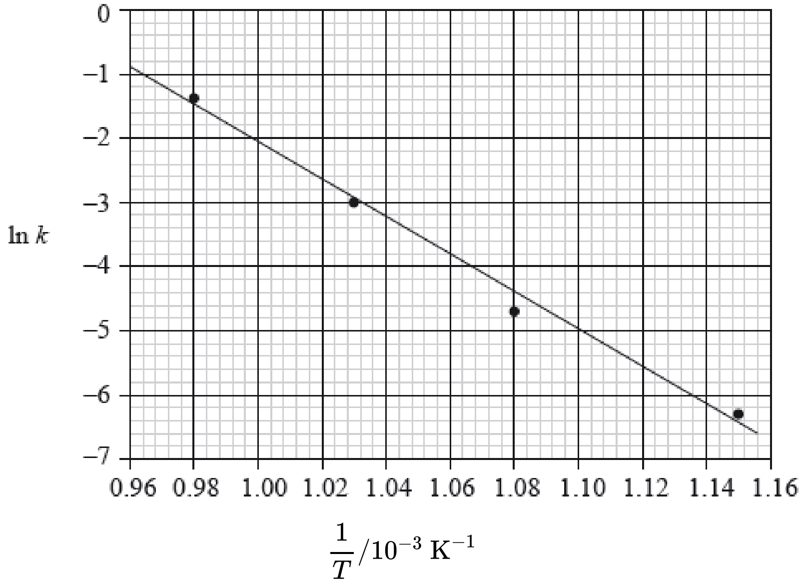
[3 marks]

Examiners report

a. [N/A]
b.i. [N/A]
b.ii. [N/A]
b.iii. [N/A]
b.iv. [N/A]
b.v. [N/A]
c. [N/A]
d. [N/A]

Consider the following graph of $\ln k$ against $\frac{1}{T}$ (temperature in Kelvin) for the second order decomposition of N_2O into N_2 and O.

$$N_2O \rightarrow N_2 + O$$



a. State how the rate constant, k varies with temperature,T. [1]

b. Determine the activation energy, E_a, for this reaction. [3]

c. The rate expression for this reaction is rate $= k[N_2O]^2$ and the rate constant is $0.244\ \mathrm{dm^3 mol^{-1} s^{-1}}$ at 750 °C. [2]

A sample of N_2O of concentration $0.200\ \mathrm{mol\,dm^{-3}}$ is allowed to decompose. Calculate the rate when 10% of the N_2O has reacted.

Markscheme

a. k increases with increase in T/k decreases with decrease in T;

Do not allow answers giving just the Arrhenius equation or involving lnk relationships.

b. $\text{gradient} = -E_a/R$;

$-30000\ (K) = -E_a/R$;

Allow value in range –28800–31300 (K).

c. $0.9 \times 0.200 = 0.180\ (\mathrm{mol\,dm^{-3}})$;

$\mathrm{rate} = \left(0.244 \times (0.180)^2 =\right)\ 7.91 \times 10^{-3}\ \mathrm{mol\,dm^{-3}s^{-1}}$;

*Award **[2]** for correct final answer.*

*Award **[1 max]** for either $9.76 \times 10^{-3}\ \mathrm{mol\,dm^{-3}s^{-1}}$ or $9.76 \times 10^{-5}\ \mathrm{mol\,dm^{-3}s^{-1}}$.*

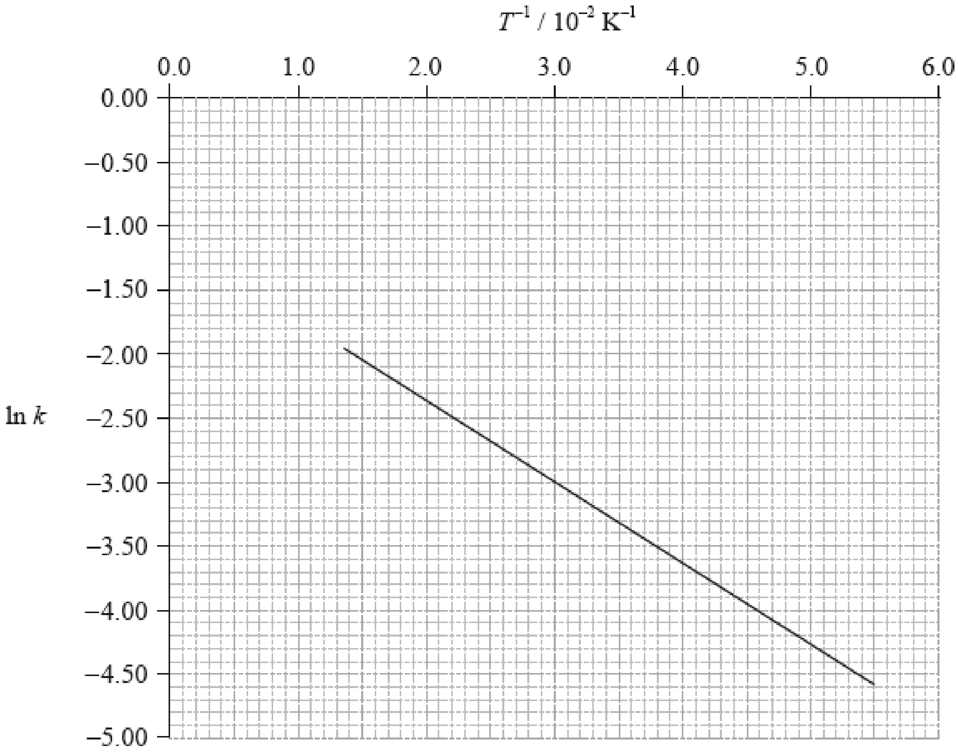
Examiners report

a. This question on chemical kinetics was very poorly answered by candidates. In (a), many candidates simply gave the Arrhenius equation and failed to describe the explicit relationship between k and T.

b. (b) was answered very poorly and although some candidates had an idea about the gradient expression, most were out by a factor of 100 in their final answer and many totally ignored units.

c. In (c), the most common error related to the 10% reduction and units also proved challenging.

To determine the activation energy of a reaction, the rate of reaction was measured at different temperatures. The rate constant, k, was determined and $\ln k$ was plotted against the inverse of the temperature in Kelvin, T^{-1}. The following graph was obtained.



a. Define the term *activation energy*, E_a. [1]

b. Use the graph on page 8 to determine the value of the activation energy, E_a, in $\mathrm{kJ\,mol^{-1}}$. [2]

c. On the graph on page 8, sketch the line you would expect if a catalyst is added to the reactants. [1]

Markscheme

a. minimum energy needed to react/start a reaction / energy difference between reactants and transition state;

b. *gradient of the line*: –63;

Accept –60 to –65.

$E_a\ (= -R \times \text{gradient}) = 0.52\ (\text{kJ mol}^{-1})$;

Accept 0.50 to 0.54.

c. gradient of the line less steep (less negative);

Accept any position as long as gradient less steep.

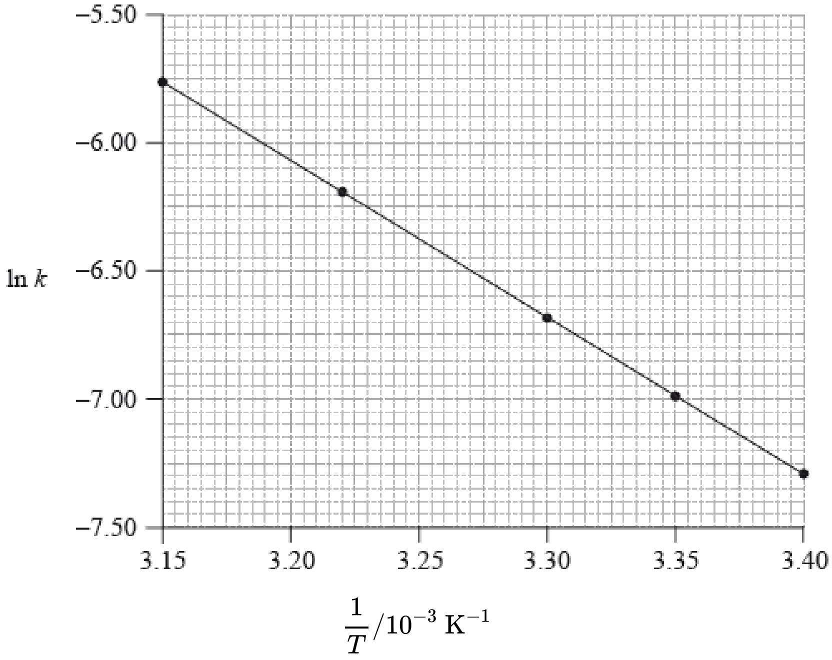
Examiners report

a. The idea of activation energy being a *minimum* was seldom communicated. Few were able to follow through all the mathematics to find E_a by a graphical method and those that did had often omitted 10^{-2} in their calculations. The answers were often poorly set out so it was difficult to assess the award of part marks; indeed, many candidates seemed to hope that a correct answer would somehow emerge from a mass of incomprehensible figures.

b. The idea of activation energy being a *minimum* was seldom communicated. Few were able to follow through all the mathematics to find E_a by a graphical method and those that did had often omitted 10^{-2} in their calculations. The answers were often poorly set out so it was difficult to assess the award of part marks; indeed, many candidates seemed to hope that a correct answer would somehow emerge from a mass of incomprehensible figures.

c. The idea of activation energy being a *minimum* was seldom communicated. Few were able to follow through all the mathematics to find E_a by a graphical method and those that did had often omitted 10^{-2} in their calculations. The answers were often poorly set out so it was difficult to assess the award of part marks; indeed, many candidates seemed to hope that a correct answer would somehow emerge from a mass of incomprehensible figures. The gradient of the graph for (c) was generously marked; all candidates had to do was to realize that the catalyst would lower the activation energy and thus the gradient would be less negative. As long as a line with less negative gradient was drawn, the mark was awarded.

Consider the following graph of $\ln k$ against $\frac{1}{T}$.



a. A catalyst provides an alternative pathway for a reaction, lowering the activation energy, E_a. Define the term *activation energy*, E_a. [1]

b. State how the rate constant, *k* , varies with temperature, *T*. [1]

c. Determine the activation energy, E_a, correct to **three** significant figures and state its units. [3]

Markscheme

a. minimum energy needed (by reactants/colliding particles) to react/start/initiate a reaction / for a successful collision;

Allow energy difference between reactants and transition state.

b. *k* increases with *T*;

Do not accept k proportional to T or statement of Arrhenius equation from Data booklet.

c. slope/gradient/$m = \frac{-E_a}{R} / -6.20 \times 10^3$;

Allow range of m from –5.96 × 10^3 to –6.44 × 10^3.

Award M1 for $m = \frac{-E_a}{R}$ *even if gradient is out of range.*

$E_a = (6.20 \times 10^3 \times 8.31) = 51.5\ \mathrm{kJ\,mol^{-1}} / 5.15 \times 10^4\ \mathrm{J\,mol^{-1}}$

E_a value correct;

units correct;

Award ***[3]*** *for correct final answer.*

Allow range of E_a *from 49.5 to 53.5 kJ* mol^{-1} */ 4.95 ×* 10^4 *to 5.35 ×* 10^4 *J* mol^{-1}.

Answer must be given correct to three significant figures.

M3 can be scored independently.

Examiners report

a. In (a) the most common mistake was for students to omit minimum in the definition of activation energy. Many described the relation between temperature and rate constant as linear or ‘proportional’. Only a small number of students gained full marks for the determination of activation energy because many either calculated an incorrect gradient or used the wrong units.

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

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

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

Reaction B is much faster than reaction A, so the iodine, $\mathrm{I_2}$, formed in reaction A immediately reacts with thiosulfate ions, $\mathrm{S_2O_3^{2-}}$, 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 ($\mathrm{H_2O_2}$)

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

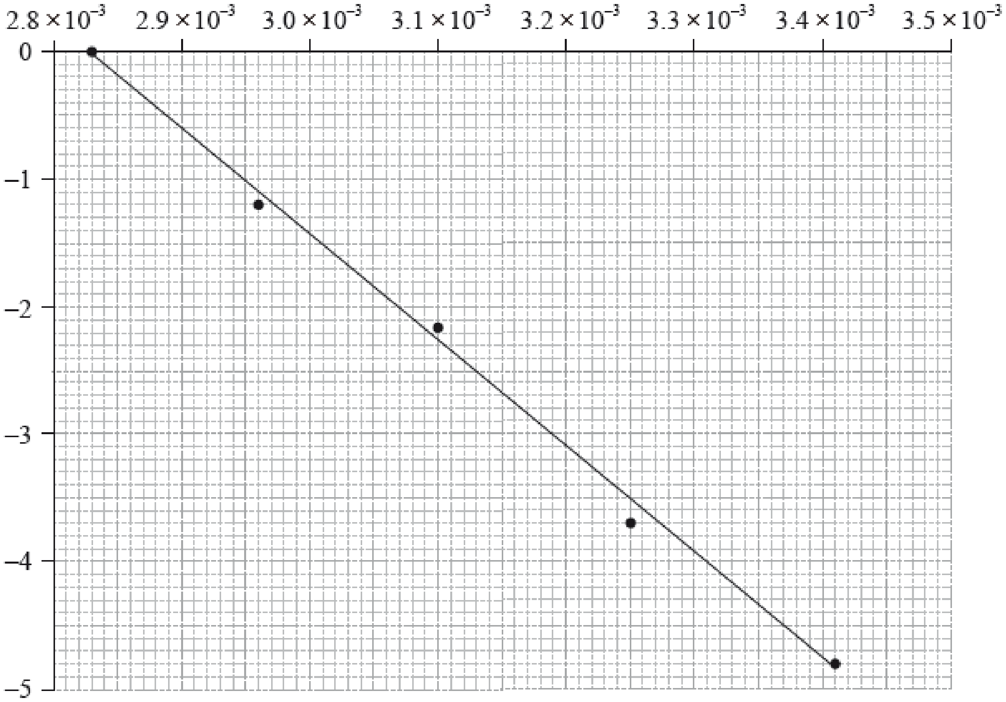
20.0 ± 0.1 $\mathrm{cm^3}$ of 1.00 $\mathrm{mol\,dm^{-3}}$ sulfuric acid ($\mathrm{H_2SO_4}$)

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

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, $\mathrm{H_2O_2}$, 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 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 $1.00 \times 10^{-4}\ \mathrm{mol}$ 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]

Markscheme

a. KI/I^-/potassium iodide/iodide (ion) (rapidly) reformed (in second stage of reaction);

b. amount (in mol) of H_2O_2/hydrogen peroxide $\gg$ amount (in mol) $Na_2S_2O_3/S_2O_3^{2-}$/sodium thiosulfate/ thiosulfate (ion);

Accept amount (in mol) of H_2O_2/hydrogen peroxide $\gg$ amount (in mol) KI/I^-/potassium iodide/iodide (ion).

Accept "H_2O_2/hydrogen peroxide is in (large) excess/high concentration".

(at end of reaction) $[H_2O_2]$ is only slightly decreased/virtually unchanged;

c. all $Na_2S_2O_3$/sodium thiosulfate/$S_2O_3^{2-}$/thiosulfate consumed/used up;

Accept "iodine no longer converted to iodide".

(free) iodine is formed / iodine reacts with starch / forms iodine-starch complex;

d.i. $(5 \times 0.1) = (\pm)0.5\ (\mathrm{cm}^3)$;

d.ii. $(\pm)0.7(\%)$;

Comprises both mass of KI = ± 0.5% and volume of KI = ± 0.2%.

d.iii. $0.5 + 0.7 = (\pm)1.2\%$;

Sum of (i) and (ii) (percentage uncertainty of total volume = absolute uncertainty as 100 cm^3).

e. total volume $0.100\ (\mathrm{dm}^3)/100\ (\mathrm{cm}^3)$;

$\left(\text{change in concentration } = \frac{1.00\times10^{-4}}{0.100} =\right)\ 1.00 \times 10^{-3}\ (\mathrm{mol\,dm}^3)$;

$\left(\text{rate} = \frac{1.00\times10^{-3}}{45} =\right)\ 2.2 \times 10^{-5}$;

*Award **[3]** for the correct final answer.*

$\mathrm{mol\,dm^{-3}s^{-1}}$;

f.i. *x-axis:* $\frac{1}{\text{Temperature}}/\frac{1}{T}/\mathrm{T}^{-1}$;

Ignore units.

y-axis: ln rate/$\log_e$ rate / ln rate constant/$\log_e$ rate constant / ln k/$\log_e k$;

f.ii. gradient $= \frac{-E_a}{R}$;

gradient $= \frac{-4.00}{(3.31\times10^{-3}-2.83\times10^{-3})} = -8333/ = \frac{-4.80}{(3.41\times10^{-3}-2.83\times10^{-3})} = -8276$;

$E_a = \left(\frac{8.31\times8333}{1000}\right) = 69.3\ (\mathrm{kJ\,mol^{-1}})/ = \left(\frac{8.31\times8276}{1000}\right) = 68.8\ (\mathrm{kJ\,mol^{-1}})$;

*Award **[3]** for correct final answer.*

Accept values from 65.0 to 73.0 kJ mol^{-1}.

*Deduct **[1]** for final answer in J mol^{-1}.*

*Deduct **[1]** for final answer not to 3 significant figures.*

g. acting as a catalyst / black powder reacts with thiosulfate ions / solid dissolves to give blue-black solution;

Accept any other valid suggestion which will make colour change more rapid.

For catalyst: amount/mass of black powder remains constant / no new/different products formed / activation energy decreased;

For other suggestions: any appropriate way to test the hypothesis;

*Award **[1]** for valid hypothesis, **[1]** for appropriate method of testing the stated hypothesis.*

Examiners report

a. This question explored basic chemical concepts in the context of a practical situation. Whilst this is one frequently carried out during practical courses, none of the questions depended on prior knowledge. Students varied significantly in their ability to interpret the information given to answer parts (a) to (c), but very few could correctly carry out the propagation of uncertainties required in part (d). An encouraging number were able to carry out the rate calculation required in part (e). It was surprising how many students, though unable to identify the axes of the Arrhenius graph given in part (f), were still able to interpret it to correctly calculate the activation energy. Part (g) was deliberately open ended and elicited a number of interesting responses, though frequently the tests proposed would not in fact confirm the suggested hypothesis.

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Consider the following reaction studied at 263 K.

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

It was found that the forward reaction is first order with respect to Cl_2 and second order with respect to NO. The reverse reaction is second order with respect to NOCl.

Consider the following equilibrium reaction.

$$Cl_2(g) + SO_2(g) \rightleftharpoons SO_2Cl_2(g) \quad \Delta H^{\ominus} = -84.5 \text{ kJ}$$

In a 1.00 dm^3 closed container, at 375 °C, 8.60×10^{-3} mol of SO_2 and 8.60×10^{-3} mol of Cl_2 were introduced. At equilibrium, 7.65×10^{-4} mol of SO_2Cl_2 was formed.

a.i. State the rate expression for the forward reaction. [1]

a.ii. Predict the effect on the rate of the forward reaction and on the rate constant if the concentration of NO is halved. [2]

a.iii. 1.0 mol of Cl_2 and 1.0 mol of NO are mixed in a closed container at constant temperature. Sketch a graph to show how the concentration of NO and NOCl change with time until after equilibrium has been reached. Identify the point on the graph where equilibrium is established. [4]

b. Consider the following reaction. [2]

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

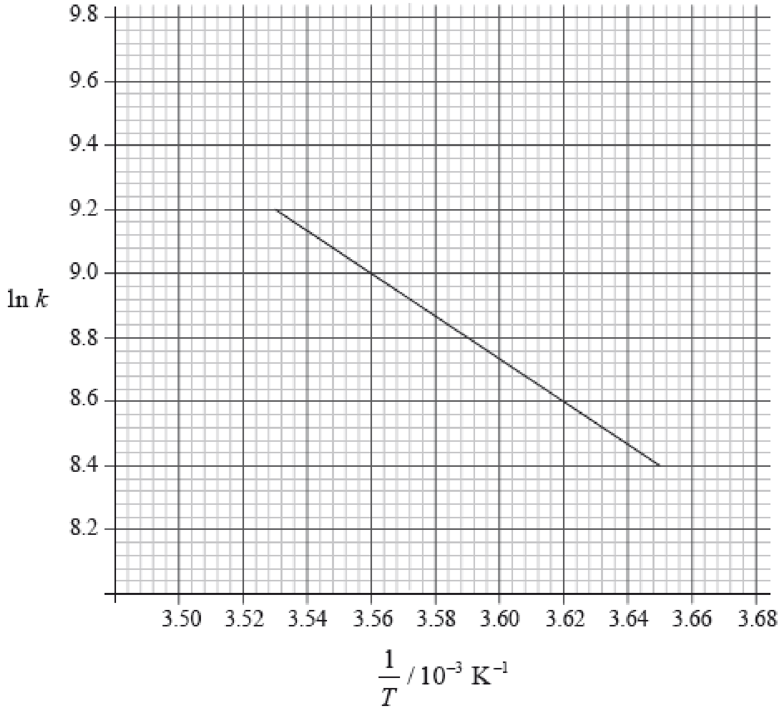
Possible reaction mechanisms are:

$$\begin{array}{lll} \text{Above 775 K:} & NO_2 + CO \rightarrow NO + CO_2 & \text{slow} \\ \text{Below 775 K:} & 2NO_2 \rightarrow NO + NO_3 & \text{slow} \\ & NO_3 + CO \rightarrow NO_2 + CO_2 & \text{fast} \end{array}$$

Based on the mechanisms, deduce the rate expressions above and below 775 K.

c. State **two** situations when the rate of a chemical reaction is equal to the rate constant. [2]

d. Consider the following graph of $\ln k$ against $\frac{1}{T}$ for the first order decomposition of N_2O_4 into NO_2. Determine the activation energy in kJ mol^{-1} for this reaction. [2]



e.i. Deduce the equilibrium constant expression, K_c, for the reaction. [1]

e.ii. Determine the value of the equilibrium constant, K_c. [3]

e.iii. If the temperature of the reaction is changed to 300 °C, predict, stating a reason in each case, whether the equilibrium concentration of SO_2Cl_2 and the value of K_c will increase or decrease. [3]

e.iv. If the volume of the container is changed to $1.50\ dm^3$, predict, stating a reason in each case, how this will affect the equilibrium concentration of SO_2Cl_2 and the value of K_c. [3]

e.v. Suggest, stating a reason, how the addition of a catalyst at constant pressure and temperature will affect the equilibrium concentration of SO_2Cl_2. [2]

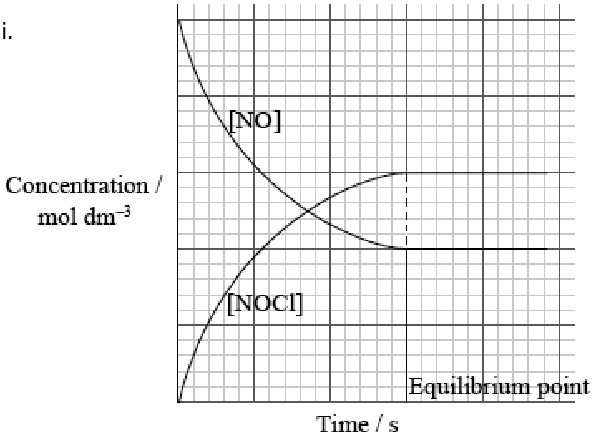
Markscheme

a.i. $\text{rate} = k[NO]^2[Cl_2]$;

a.ii. rate of reaction will decrease by a factor of 4;

no effect on the rate constant;

a.iii.



y axis labelled concentration/$mol\ dm^{-3}$ and *x* axis is labelled time/s;

gradient for [NO];

gradient for [NOCl] will be equal and opposite;

equilibrium point identified / two curves level off at same time;

b. Above 775 K: $\text{rate} = k[NO_2][CO]$;

Below 775 K: $\text{rate} = k[NO_2]^2$;

c. zero order reaction;

all concentrations are $1.0\ mol\ dm^{-3}$;

d. $\text{slope} = \frac{9.2-8.4}{(3.53-3.65)\times10^{-3}} = -6.67 \times 10^3$;

$(E_a = 6.67 \times 10^3 \times 8.31)$

$55.4\ (kJ\ mol^{-1})$;

Accept in range 55.0 – 56.0

*Award **[1]** if 55454 (J) stated*

*Award **[2]** for the correct final answer*

e.i. $(K_c) = \frac{[SO_2Cl_2]}{[Cl_2][SO_2]}$;

Ignore state symbols.

Square brackets [ ] required for the equilibrium expression.

e.ii. 7.84×10^{-3} mol of SO_2 and 7.84×10^{-3} mol of Cl_2;

$7.84 \times 10^{-3}\ mol\,dm^{-3}$ of SO_2, $7.84 \times 10^{-3}\ mol\,dm^{-3}$ of Cl_2 **and**

$7.65 \times 10^{-4}\ mol\,dm^{-3}$ of SO_2Cl_2;

12.5;

*Award **[1]** for 10.34*

*Award **[3]** for the correct final answer*

e.iii value of K_c increases;

$[SO_2Cl_2]$ increases;

decrease in temperature favours (forward) reaction which is exothermic;

Do not allow ECF.

e.iv no effect on the value of K_c / depends only on temperature;

$[SO_2Cl_2]$ decreases;

increase in volume favours the reverse reaction which has more gaseous moles;

Do not allow ECF.

e.v. no effect;

catalyst increases the rate of forward and reverse reactions (equally) / catalyst decreases activation energies (equally);

Examiners report

a.i. In part (a) the rate expression was correctly stated although some confused this with an equilibrium constant expression.

a.ii. Only the better candidates realized that the rate of reaction will decrease by a factor of four and there will be no effect on the rate constant.

a.iii Although most candidates were able to correctly sketch the concentration versus time graph many forgot to label the axes or include units.

b. Part (b) was well answered and candidates demonstrated a good understanding of rate expressions based on reaction mechanism.

c. The better candidates were able to figure out that the rate of a chemical reaction is equal to the rate constant when all concentrations are $1.0\ mol\,dm^{-3}$ or for a zero order reaction.

d. Most candidates had difficulty in calculating activation energy from the graph in part (d) and some gave the answer in $J\,mol^{-1}$ instead of $kJ\,mol^{-1}$ which showed that they missed this instruction in the question.

e.i. In part (e), the equilibrium constant expression was correctly stated by the majority but calculating the value of K_c proved to be difficult.

e.ii A large number of candidates obtained the incorrect answer of 10.34 as a result of using the initial concentrations of the reactants instead of equilibrium concentrations.

e.iii.[N/A]

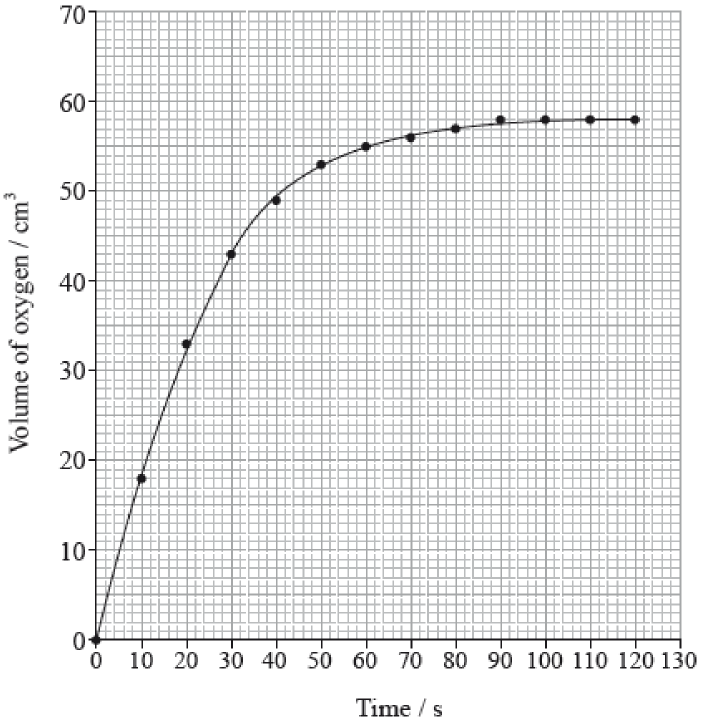
e.iv.The application of Le Chatelier's principle was handled well by the majority with minor omissions such as not using the term gaseous particles in part (iv).

e.v.Some candidates stated that the addition of a catalyst does not affect the value of K_c or the position of equilibrium, which did not answer the question and scored no marks because they had not commented on the concentration of $SOCl_2$. Some candidates correctly stated that a catalyst increases the rate of forward and reverse reactions equally.

Hydrogen peroxide decomposes according to the equation below.

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

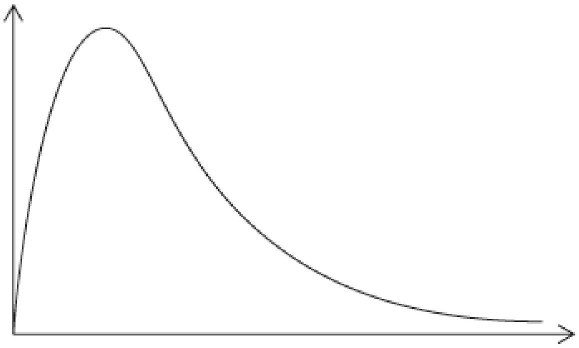
The rate of the decomposition can be monitored by measuring the volume of oxygen gas released. The graph shows the results obtained when a solution of hydrogen peroxide decomposed in the presence of a CuO catalyst.



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]



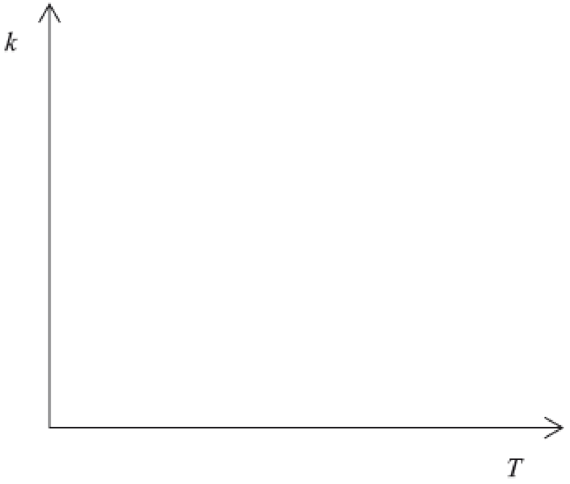
c. (i) In some reactions, increasing the concentration of a reactant does not increase the rate of reaction. Describe how this may occur. [2]

(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]

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

(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.

Markscheme

a.i. (draw a) tangent to the curve at origin/time = 0/start of reaction;

(calculate) the gradient/slope (of the tangent);

a.ii. rate decreases (with time);

concentration/number of (reactant) molecules per unit volume decreases (with time);

Do not accept “number of molecules decreases” or “amount of reactant decreases”.

collisions (between reactant molecules/reactant and catalyst) become less frequent;

Do not accept “fewer collisions” without reference to frequency (eg, no. collisions per second).

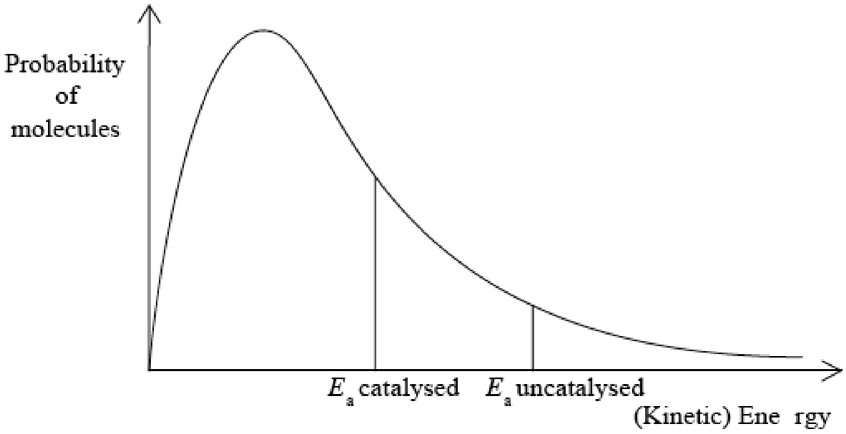
b. *y-axis*: probability / fraction of molecules/particles / probability density

Allow “number of particles/molecules” on y-axis.

and

x-axis: (kinetic) energy;

Accept “speed/velocity” on x-axis.



correct relative position of E_a catalysed and E_a uncatalysed;

more/greater proportion of molecules/collisions have the lower/required/catalysed E_a (and can react upon collision);

*M3 can be scored by stating **or** shading and annotating the graph.*

Accept “a greater number/proportion of successful collisions as catalyst reduces E_a”.

c. (i) reactant not involved in (or before) the slowest/rate-determining step/RDS;

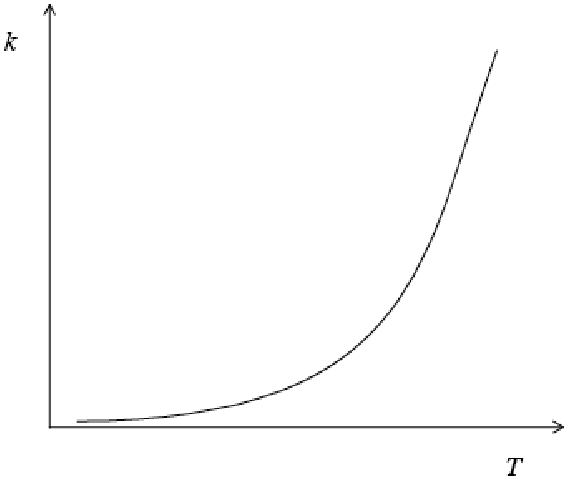
reactant is in (large) excess;

(ii) $(\mathrm{rate} =)\ k[\mathrm{A}]$;

Accept rate = $k[A]^1[B]^0$.

d. curve with a positive slope curving upwards;

Do not penalize if curve passes through the origin.



e. (i) heat transferred/absorbed/released/enthalpy/potential energy change when 1 mol/molar amounts of reactant(s) react (to form products) / *OWTTE*;

under standard conditions / at a pressure 100 kPa/101.3 kPa/1 atm **and** temperature 298 K/25 °C;

*Award **[2]** for difference between standard enthalpies of products and standard enthalpies of reactants /* $H^\ominus$ *(products) –* $H^\ominus$ *(reactants).*

*Award **[2]** for difference between standard enthalpies of formation of products and standard enthalpies of formation of reactants /* $\Sigma\Delta H_f^\ominus$ *(products) –* $\Sigma\Delta H_f^\ominus$ *(reactants).*

(ii) $(1.00 \times 0.0500 =)\ 0.0500\ (\text{mol})$;

$(0.0500 \times 57.9 =)\ 2.90\ (\text{kJ})$;

Ignore any negative sign.

*Award **[2]** for correct final answer.*

*Award **[1 max]** for 2900 J.*

(iii) $\left(\frac{2.50}{40.00} =\right)\ 0.0625\ (\text{mol NaOH})$;

$0.0500 \times 4.18 \times 13.3 = 2.78\ (\text{kJ}) / 50.0 \times 4.18 \times 13.3 = 2780\ (\text{J})$;

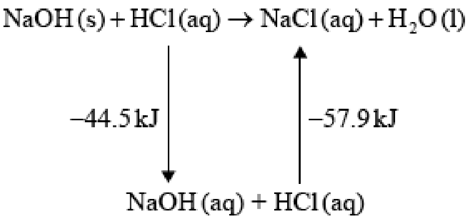
$\left(\frac{2.78}{0.0625}\right) = -44.5\ (\text{kJ mol}^{-1})$;

*Award **[3]** for correct final answer.*

Negative sign is necessary for M3.

Award M2 and M3 if is used to obtain an enthalpy change of –46.7 (kJ mol^{-1}).

(iv) $-44.5 - 57.9$ / correct Hess's Law cycle (as below) / correct manipulation of equations;



-102.4 kJ;

*Award **[2]** for correct final answer.*

f. (i) zinc (only) forms the ion Zn^{2+} / has the oxidation state $+2$;

Allow forms only one ion / has only one oxidation state.

has full d-subshell/orbitals / does not have a partially filled d-subshell/orbitals (needed to exhibit transition metal properties);

(ii) Fe^{2+}: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^6 / [\text{Ar}]\ 3\text{d}^6$ **and** Fe^{3+}: $1\text{s}^2 2\text{s}^2 2\text{p}^6 3\text{s}^2 3\text{p}^6 3\text{d}^5 / [\text{Ar}]\ 3\text{d}^5$;

half-full sub-level/3d^5 has extra stability;

less repulsion between electrons / electrons singly occupy orbitals / electrons do not have to pair with other electrons;

Accept converse points for Fe^{2+}.

Examiners report

a.i. Most candidates related the rate of reaction to the gradient of the curve, but only a few suggested drawing a tangent at $t = 0$.

a.ii. Answers were often disappointing and only a few candidates gained full marks.

Candidates often talked about the number of reactant molecules decreasing but neglected to relate this to a lower concentration. Also some candidates still fail to highlight frequency rather than the number of collisions.

b. Well answered by more than half of the candidates. The labelling of the axes was a challenge for some candidates. The annotation of the diagram with the energy of activation with and without a catalyst was mostly correct, though some weaker students confused it with the effect of temperature and constructed a second curve. Some candidates could not offer an explanation for the third mark.

c. (i) Only a few candidates scored this mark. Many candidates stated that a reactant concentration having no effect indicated that the reaction that was zero order in that species, rather than describing the underlying mechanistic reason for the zero order dependence.

(ii) More than half of the candidates could construct a correct rate expression from information about the order of the reactants.

d. A number of candidates gave a linear relationship, rather than an exponential one, between reaction rate and temperature.

e. (i) Defining the standard enthalpy change of reaction was not well answered.

(ii) More than half of the candidates calculated the amount of energy released correctly.

(iii) Half of the candidates were able to gain the three marks. Many candidates lost the third mark for not quoting the negative sign for the enthalpy change. Quite a few candidates used a wrong value for the mass of water.

(iv) Many good answers. A Hess's Law cycle wasn't often seen. Quite a few candidates scored through ECF from (iii).

f. (i) Most candidates knew that zinc has a full 3d sub-shell but almost all missed out on the second mark about only having one possible oxidation state in its compounds.

(ii) This was a challenging question for many candidates. A large number of candidates did not give the correct electron configurations for the ions, and only few mentioned the stability of the half-full d-sub-shell. Very few scored the third mark.

A student used a pH meter to measure the pH of different samples of water at 298 K.

Sample	pH ± 0.1
Rain water	5.1
River water	4.4
Tap water	6.5
Bottled water	7.1

a. Use the data in the table to identify the most acidic water sample. [1]

b. Calculate the percentage uncertainty in the measured pH of the rain water sample. [1]

c. Determine the ratio of $[\mathrm{H}^+]$ in bottled water to that in rain water. [2]

$$\frac{[H^+]\ in\ bottled\ water}{[H^+]\ in\ rain\ water}$$

d. Determine the concentration of hydroxide ions in the sample of river water. [2]

e. The acidity of non-polluted rain water is caused by dissolved carbon dioxide. State an equation for the reaction of carbon dioxide with water. [1]

Markscheme

a. river (water);

b. $\left(\frac{0.1}{5.1} \times 100 =\right)\ 2\%$;

c. recognition that values differ by 2 pH units / calculation of **both** $[\mathrm{H}^+]$ values;

$(\mathrm{ratio} =)\ 1 : 100/\frac{1}{100}/10^{-2}/0.01$;

*Award **[2]** for correct final answer.*

*Award **[1 max]** for 100:1/100/10^2.*

d. $\mathrm{pOH} = (14.0 - 4.4 =)\ 9.6/[\mathrm{H}^+] = 4 \times 10^{-5}\ (\mathrm{mol\,dm^{-3}})$;

Accept $[H^+] = 3.98 \times 10^{-5}$ (mol dm^{-3}).

$[\mathrm{OH}^-] = 3 \times 10^{-10}\ (\mathrm{mol\,dm^{-3}})$;

Accept 2.51×10^{-10} (mol dm^{-3}).

*Award **[2]** for correct final answer.*

e. $\mathrm{CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+/CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_2O^+/CO_2 + H_2O \rightleftharpoons H_2CO_3}$;

Do not penalize missing reversible arrow.

Do not accept equations with the carbonate ion as a product.

Examiners report

a. A very well answered question.

b. The majority of candidates calculated the percentage uncertainty correctly, however, more than half of them did not pay attention to stating the answer to the appropriate number of significant figures. Some candidates used river water data instead of rain water.

c. More than half of the candidates calculated the correct ratio of hydrogen ion concentration. The majority of these candidates calculated the concentration of hydrogen ions in both samples, instead of simply using the difference of 2 pH units.

d. Generally well answered. Some students only scored one mark, stopping at the calculation of the pOH or the concentration of hydrogen.

e. About half the candidates wrote correct products, however, most of the candidates did not use reversible arrows. Several variations of incorrect products were given including $\mathrm{H_2O_2}$ and CO.

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]

Markscheme

a. $\mathrm{M(CH_3COOH)}\ (= (4 \times 1.01) + (2 \times 12.01) + (2 \times 16.00)) = 60.06\ (\mathrm{g\,mol^{-1}})$;

Accept 60 (g mol^{-1}).

$\mathrm{mass\ (CH_3COOH)}\ (= 5.00 \times 1.05) = 5.25\ (\mathrm{g})$;

$\frac{5.25}{60.06} = 0.0874\ (\mathrm{mol})$;

*Award **[3]** for correct final answer.*

Accept 0.0875 (comes from using Mr = 60 g mol^{-1}).

b. percentage uncertainty in volume of ethanoic acid $= 100 \times \frac{0.05}{5.00} = 1\%$;

percentage uncertainty in total volume $= 100 \times \frac{0.62}{50} = 1.24\%$;

total percentage uncertainty $= 1 + 1.24 = 2.24\%$;

Accept rounding down to 2.2/2%.

c.i. $\pm 0.1/0.10\ (\mathrm{cm^3})$;

*Do **not** accept without ±.*

c.ii. $26.00\ (\mathrm{cm^3})$;

c.iii $26.00 - 3.00 = 23.00\ (\mathrm{cm^3})$;

*If other methods used, award **M1** for calculating amount of NaOH reacting with CH_3COOH.*

$0.200 \times \frac{23.00}{5.00} = 0.920\ (\mathrm{mol\,dm^{-3}})$;

*Award **[2]** for correct final answer.*

If (ii) given as mean titre (26.5 cm^3) then ECF answer comes to 0.94 (mol dm^{-3}).

c.iv $(K_c =)\frac{[\mathrm{CH_3COOC_2H_5}][\mathrm{H_2O}]}{[\mathrm{C_2H_5OH}][\mathrm{CH_3COOH}]}$;

Do not penalize minor errors in formulas.

Accept $(K_c =)\frac{[esther][water]}{[ethanol/alcohol][(ethanoic)\ acid]}$.

c.v. $(K_c =)\frac{0.828 \times 1.80}{0.884 \times 0.920} = 1.83$;

If assumed [CH_3COOH] = 0.884 mol dm^{-3}, answer is 1.91 – allow this even if an answer was obtained for (iii).

If (ii) given as mean titre (26.5 cm^3) then ECF answer comes to 1.79.

d. repeat the titration a day/week later (and result should be the same) / *OWTTE*;

Accept "concentrations/physical properties/macroscopic properties of the system do not change".

e. enthalpy change/ΔH for the reaction is (very) small / *OWTTE*;

f. decreases (the amount of ethanoic acid converted);

Accept "increases amount of ethanoic acid present <u>at equilibrium</u>" / OWTTE.

(adding product) shifts position of equilibrium towards reactants/LHS / increases

the rate of the reverse reaction / *OWTTE*;

g. ethyl ethanoate/$\mathrm{CH_3COOC_2H_5}$/ester;

forms only weak hydrogen bonds (to water);

Allow "does not hydrogen bond to water" / "hydrocarbon sections too long" / OWTTE.

M2 can only be given only if M1 correct.

h. (large excess of) water will shift the position of equilibrium (far to the left) / *OWTTE*;

Accept any other chemically sound response, such as "dissociation of ethanoic acid would affect equilibrium".

Examiners report

a. Generally candidates found this question quite challenging and some left quite a number of parts unanswered. The tradition is that the first question on the paper is a data response question, which often addresses many aspects of the syllabus, and unfortunately candidates, especially those of average or below average ability, seem to have difficulty in tackling questions of this nature. One other issue with data response questions is that, of necessity, the data appears at the beginning of the question whilst, mainly because of the space left for candidates to answer, the later parts of the question referring to these data may not appear until a number of pages into the paper.

Part (a) concerning density, volume and amount of substance was generally reasonably well answered, but the following parts, concerning uncertainties, were rarely answered correctly and a number confused precision (uncertainty, either absolute or as a percentage) and accuracy (percentage error in the value obtained). Many candidates also seemed to lack experimental common sense, simply taking an average that included an initial titre that was much larger than the concordant second and third titres, rather than excluding it. This lack of experimental "know how" was also evident in responses to (c) (iii) where it was unusual for the approach to the question to indicate the candidate had realised that the alkali was neutralising two different acids (HCl and $\mathrm{CH_3COOH}$) and again in part (d) where it was rare for the response to outline a practical solution to the problem, though quite a number of candidates suggested that the pH would become constant, presumably not realising that the pH would be dominated by the HCl catalyst. Most students could however carry out the more routine tasks of writing an equilibrium constant expression and determining its value from the data given. Many candidates were aware of Le Chatelier effects on the position of equilibrium, but a significant number failed to use this information to answer the question actually asked and the unusual approach to the effect of temperature disconcerted many. Whilst most students managed to identify the ester as the component of the mixture that was insoluble in water, the reasons given were usually couched in terms of the polarity of the molecule (many quite polar molecules, halogenoalkanes for example, are insoluble in water) rather than its inability to form strong hydrogen bonds to water, which is the critical factor. Quite a number of students came up with a valid reason why water would not be a suitable solvent, though some students appeared to have overlooked the fact the question stated "other reason".

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Bromomethane was used as a pesticide until it was found to be ozone-depleting.

a. State the equation for the reaction between methane and bromine to form bromomethane. [1]

b.i. Explain, using equations, the complete free-radical mechanism for the reaction of methane with bromine, including necessary reaction conditions. [4]

b.ii. Bromomethane reacts with aqueous sodium hydroxide. State the organic product of this reaction. [1]

c. Explain why the rate of the reaction between iodomethane, CH_3I, and NaOH(aq) is faster than the rate of the reaction between CH_3Br and NaOH(aq). [2]

d.i. Bromine can be produced by the electrolysis of **molten** sodium bromide. [2]

Deduce the half-equation for the reaction at each electrode.

Positive electrode (anode):

Negative electrode (cathode):

d.ii. Predict the products formed at the electrodes during the electrolysis of concentrated **aqueous** sodium bromide. [2]

Positive electrode (anode):

Negative electrode (cathode):

e. Bromine reacts with aqueous sodium iodide. [1]

$$Br_2(aq) + 2NaI(aq) \rightarrow I_2(aq) + 2NaBr(aq)$$

Identify the oxidizing agent in this reaction.

f.i. Define the term *standard electrode potential, $E^{\ominus}$*. [1]

f.ii. Draw a labelled diagram for the voltaic cell in which the following reaction occurs. [4]

$$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$$

Include in your answer the direction of electron flow and the polarity of the electrodes.

f.iii.A student measures a voltage of 2.65 V in the voltaic cell formed between magnesium and copper half-cells using a digital voltmeter. [2]

State the random uncertainty of this value, in V, and the number of significant figures in the answer.

Random uncertainty:

Significant figures:

f.iv.Outline how the student can reduce the random error in her results. [1]

g. Determine the standard enthalpy change of formation, $\Delta H_{\mathrm{f}}^{\Theta}$, of NaCl(s), in $\mathrm{kJ\ mol^{-1}}$, using a Born-Haber cycle and tables 7, 10 and 13 of the data booklet. The standard enthalpy change of atomization (standard enthalpy change of sublimation), $\Delta H_{\mathrm{at}}^{\Theta}$, of Na(s) is $+108\ \mathrm{kJ\ mol^{-1}}$. [4]

Markscheme

a. $\mathrm{CH_4 + Br_2 \rightarrow CH_3Br + HBr}$;

b.i.*Initiation:*

$\mathrm{Br_2} \xrightarrow{\mathrm{UV}/hf/hv} \mathrm{2Br\bullet}$;

Reference to UV/light or high temperatures must be included.

Propagation:

$\mathrm{Br\bullet + CH_4 \rightarrow CH_3\bullet + HBr}$;

$\mathrm{CH_3\bullet + Br_2 \rightarrow CH_3Br + Br\bullet}$;

Termination:

*Award **[1 max]** for any one of:*

$\mathrm{Br\bullet + Br\bullet \rightarrow Br_2}$;

$\mathrm{CH_3\bullet + Br\bullet \rightarrow CH_3Br}$;

$\mathrm{CH_3\bullet + CH_3\bullet \rightarrow C_2H_6}$;

Allow representation of radical without • (eg Br, CH_3) if consistent throughout mechanism.

*Award **[3 max]** if initiation, propagation and termination are not stated or are incorrectly labelled for equations.*

b.ii.$\mathrm{methanol/CH_3OH}$;

c. C–I bond is weaker than the C–Br bond so more easily broken;

C–I bond is longer than the C–Br bond / I larger than Br so bonding electrons not as tightly held / $\mathrm{I^-}$ is better leaving group than $\mathrm{Br^-}$;

d.i.*Positive electrode (anode):*

$\mathrm{2Br^- \rightarrow Br_2(g) + 2e^- / Br^- \rightarrow \frac{1}{2}Br_2(g) + e^-}$;

Negative electrode (cathode):

$\mathrm{Na^+ + e^- \rightarrow Na(l)}$;

*Award **[1 max]** for correct equations at incorrect electrodes.*

Ignore state symbols.

Accept e *instead of* $\mathrm{e^-}$.

Penalize use of equilibrium signs once only.

d.ii *Positive electrode (anode):*

bromine/Br_2;

Negative electrode (cathode):

hydrogen/H_2;

Allow sodium hydroxide/NaOH/hydroxide/OH^- formation.

e. bromine/Br_2;

Do not accept bromide/Br^-.

f.i. potential of reduction half-reaction under standard conditions measured relative to standard hydrogen electrode/SHE/potential under standard conditions relative to standard hydrogen electrode/SHE;

Instead of standard state allow either solute concentration of $1 mol\, dm^{-3}$ or

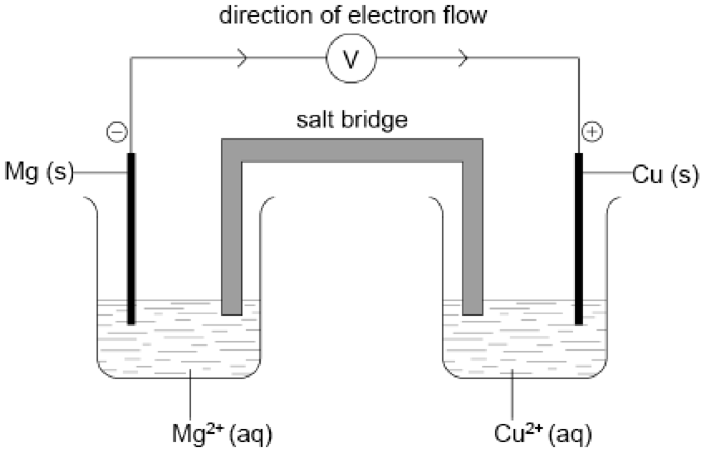
$100kPa/1.00 \times 10^5 Pa$ for gases.

Allow 1 bar for $100kPa/1.00 \times 10^5 Pa$.

Allow 1 atm.

Allow voltage instead of potential.

f.ii.



correct diagram including (voltmeter), 4 correct species (state symbols not required) and connecting wires;

No credit if wires to electrodes immersed in the solutions.

Accept ammeter/meter/lamp instead of voltmeter.

labelled salt bridge;

Accept an appropriate salt (name or formula) instead of salt bridge (eg, potassium nitrate).

correctly labelled electrodes as +/cathode **and** –/anode;

flow of electrons from Mg to Cu in external circuit;

f.iii *Random uncertainty:* (±) 0.01 (V);

Significant figures: 3;

f.iv. repeat readings **and** take an average / use more precise equipment;

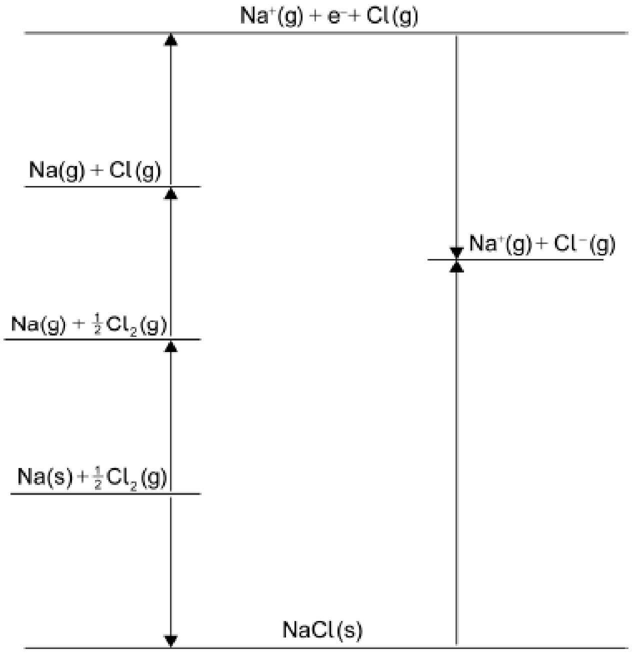
g. $\text{atomization of chlorine} = \frac{1}{2}\text{ bond enthalpy } / \frac{1}{2}\ 243\ /\ 121.5\ (\text{kJ mol}^{-1})$;

correct values for *ionization* Na ($+496\ \text{kJ mol}^{-1}$) **and** *electron affinity* Cl ($-349\ \text{kJ mol}^{-1}$)

and lattice enthalpy of NaCl ($+790\ \text{kJ mol}^{-1}\ /+769\ \text{kJ mol}^{-1}$);

Born-Haber energy cycle;

Accept lines or arrows in energy cycle.



$\Delta H_f^{\ominus}(\text{NaCl(s)}) = -413.5 \;/ -413 \;/ -414\ (\text{kJ mol}^{-1})$;

Accept $-392.5/-392/-393 if +769$ *used for lattice enthalpy.*

*Award **[4]** for correct final answer.*

Examiners report

a. Candidates found it difficult to write the equation in (a) and the mechanisms in (b) (i) ranged from really good to no understanding. Many opined the production of $\bullet\text{H}$ in the first propagation step. A significant number of candidates suggested a mechanism involving ions despite *free radical* begin stated in the stem. Most were able to give methanol in (ii). Few scored full marks for (c); the answer needed to be thought through carefully. In (d) the electrodes were often reversed or the equations unbalanced. Few understood the significance of the water present in the answers to (ii). A high percentage of candidates gave the correct answer to (e) but (f) was poorly answered. Either the standard hydrogen electrode or standard conditions were omitted in (i) and the standard of diagrams in (ii) was very poor indeed. Little care seemed to have been taken over their presentation; it was not clear what, if anything, was in the beakers and electrode connections were shown actually in the solutions. In (iii) some did not notice that the voltmeter was digital but most gave the number of significant figures correctly. In (iv) many suggested repeated readings but few stated that an average omitted must be taken. In (g), those who didn't draw out the cycle tended to get the answer wrong. Examiners cannot give part marks if they cannot work out what is being done. There was one mark for a correct Born-Haber cycle. Very few gained the mark for dividing the chlorine value by 2.

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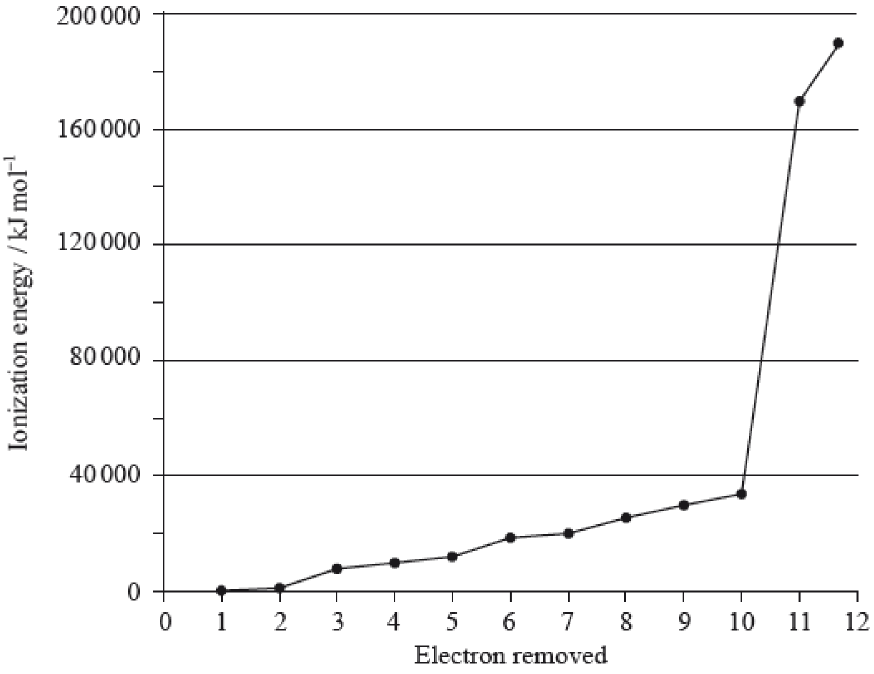
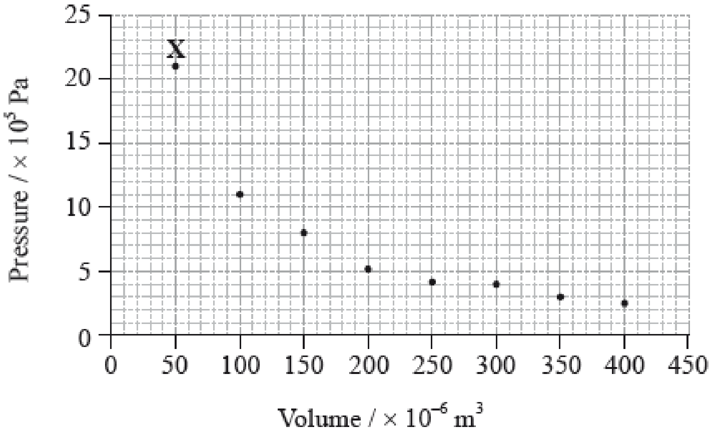
A sample of magnesium contains three isotopes: magnesium-24, magnesium-25 and magnesium-26, with abundances of 77.44%, 10.00% and 12.56% respectively.

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.

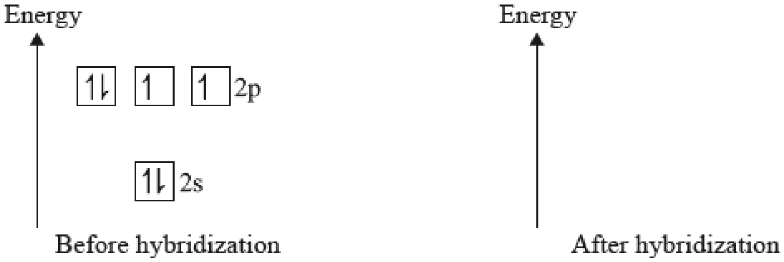
c. (i) Magnesium reacts with oxygen to form an ionic compound, magnesium oxide. Describe how the ions are formed, and the structure and bonding in magnesium oxide. [4]

(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 CO_2. [7]

(ii) Sketch the orbitals of an oxygen atom in 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.

Markscheme

a. (i) $\left(\frac{(77.44\times24)+(10.00\times25)+(12.56\times26)}{100}\right)$;

24.35;

*Award **[2]** for correct final answer.*

Two decimal places are required for M2.

Do not award any marks for 24.31 without showing method (as the value can be copied from the Data Booklet).

(ii) same atomic radii / 160 pm;

isotopes only differ by number of neutrons/size of nucleus / radius determined by electron shells and number of protons / *OWTTE*;

Accept neutrons do not affect distance of electrons / OWTTE.

b. (i) decreasing repulsion between electrons / radius decreases as electrons are removed;

Accept increasing positive charge on ion attracts electrons more strongly.

(ii) 10th electron is in second energy level/shell while 11th electron is in first energy level/shell / 10th is removing electron from electronic arrangement 2,1 while 11th ionization energy is removing electron from electronic arrangement 2;

11th electron removed is much closer to the nucleus / 11th electron removed from a (much) lower energy level/shell;

Accept opposite statement for 10th electron.

c. (i) magnesium (atom) gives two electrons to oxygen (atom) / oxygen (atom) takes two electrons from magnesium (atom) / magnesium (atom)

loses two electrons **and** oxygen (atom) gains two electrons;

3-dimensional/3-D arrangement of ions / lattice of ions;

(electrostatic) attraction between oppositely charged ions/Mg^{2+} and O^{2-};

(ii) electrostatic attraction between a pair of electrons and (positively charged) nuclei;

Accept a/two pairs of shared electrons.

(iii) difference in electronegativity is larger between Mg and O/smaller between C and O;

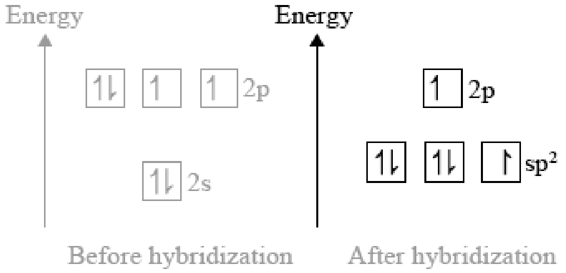
Accept reference to a numerical value of difference in electronegativity such as above and below 1.80.

d. (i) C: sp hybridization;

O: sp^2 hybridization;

*Award **[1]** if the answer is sp without specifying C or O atoms.*

(ii)



three sp^2 orbitals **and** one p-orbital at higher energy;

sp^2 orbitals contain: two, two and one electron **and** p-orbital contains one electron;

Do not allow ECF from (d)(i).

(iii) ability of atom/nucleus to attract bonding/shared pair of electrons / attraction of nucleus for bonding/shared pair of electrons / *OWTTE*;

(iv) (same number of shells but) increase in nuclear charge/atomic number/number of protons increases electronegativity / O has more protons than C;

Accept oxygen has a higher effective nuclear charge.

decrease in radius along the period increases electronegativity / O has smaller radius than C;

e. (i) smooth curve through the data;

*Do not accept a curve that passes through **all** of the points or an answer that joins the points using lines.*

(ii) $p = 21 \times 10^5 / 2.1 \times 10^6\ (\mathrm{Pa}) / 2.1 \times 10^3\ (\mathrm{kPa})$ **and**

$V = 50 \times 10^{-6} / 5.0 \times 10^{-5}\ (\mathrm{m}^3) / 5.0 \times 10^{-2}\ (\mathrm{dm}^3)$;

$\left(n = \frac{pV}{RT}\right) \frac{2.1 \times 10^6 \times 5.0 \times 10^{-5}}{8.31 \times 330}$;

$n = 0.038\ (\mathrm{mol})$;

*Award **[3]** for correct final answer.*

For M3 apply ECF for correct computation of the equation the student has written, unless more than one mistake is made prior this point.

f. (i) equilibrium between HIn and $\mathrm{In}^- / \mathrm{HIn} \rightleftharpoons \mathrm{In}^- + \mathrm{H}^+$;

the colours of HIn and In^- are different;

if added to acid, the equilibrium shifts to the left and the colour of HIn is seen / *OWTTE*;

if added to base/alkali, the equilibrium shifts to the right and the colour of In^- is seen / *OWTTE*;

(ii) phenolphthalein;

Accept phenol red.

Examiners report

a. (i) Most candidates were able to calculate the relative atomic mass to the correct number of decimal places.

(ii) Only strong candidates were able to predict the same radius for the isotopes and gave correct reasoning. However, the majority of candidates predicted that a larger number of neutrons resulted is a smaller radius, reflecting a poor understanding of atomic structure.

b. (i) Very few candidates were able to explain the increase in successive ionization energies for electrons removed from the same sub-shell. Many candidates gave incorrect reasoning.

(ii) The increase between the 10th and 11th ionization energies of magnesium was explained correctly by about half of the candidates. Few candidates scored the first mark by identifying the correct shells or sub-shells the electrons are removed from.

c. (i) Well answered by many candidates. A few candidates were confusing ionic with covalent bonding, and some referred to a linear MgO molecule in an ionic lattice.

(ii) Few candidates were able to describe the covalent bond precisely. Those who didn't score usually didn't make any reference to pairs of electrons.

(iii) Many candidates obtained this mark with satisfactory arguments. It was disappointing to see the abundance of answers based on "is a metal with a non-metal" or "both are non-metals".

d. (i) A few candidates identified sp hybridization based on a linear structure. Only the strongest candidates were able to give the correct hybridization for oxygen as well.

(ii) This was the most challenging question on the paper. It was rare to see a correct answer. It seems candidates did not have a good understanding of hybridization.

(iii) Less than half the candidates were able to define electronegativity precisely. Many candidates did not relate it to the pair of electrons in a covalent bond, and simply talked about attracting electrons, which was not sufficient for the mark.

(iv) Many candidates gained the first mark by stating that oxygen has more protons than carbon. But very few candidates identified the second factor, which is the smaller radius of oxygen.

e. (i) More than half of the candidates drew a smooth curve that was central to the data points. Errors included straight lines, curves joining all data points, or a curve that was not central to the points.

(ii) A very well answered question. Some candidates converted the units of *p* and *V* incorrectly and others did not read the scales of the graph correctly.

f. (i) Many candidates could explain the behaviour of indicators, but there were also some poor answers that did not acknowledge the importance of equilibrium in the action of an indicator.

(ii) Most candidates suggested a suitable indicator.

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

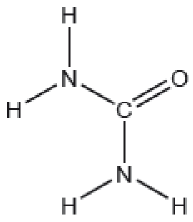
Urea can also be made by the direct combination of ammonia and carbon dioxide gases.

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

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]

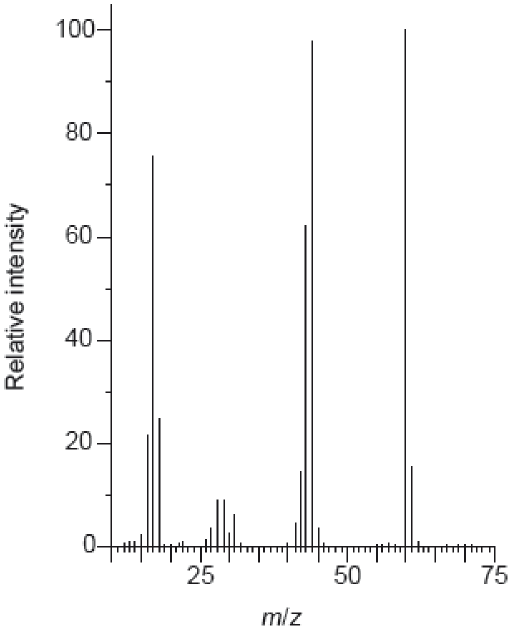
Formulate a balanced equation for the reaction.

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]



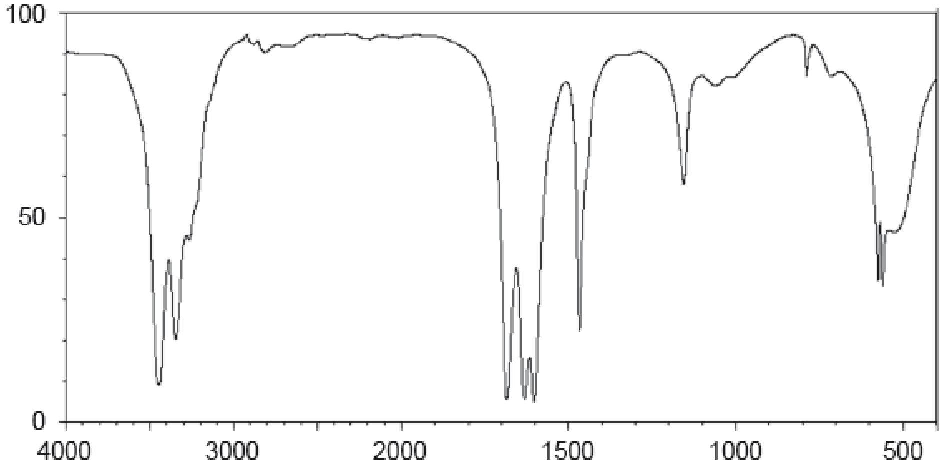
[Source: http://sdbs.db.aist.go.jp]

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]



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

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]

Markscheme

a.i. molar mass of urea «$4 \times 1.01 + 2 \times 14.01 + 12.01 + 16.00$» = 60.07 «g mol^{-1}»

«% nitrogen = $\frac{2\times14.01}{60.07} \times 100$ =» 46.65 «%»

*Award **[2]** for correct final answer.*

*Award **[1 max]** for final answer not to two decimal places.*

[2 marks]

a.ii. «cost» increases ***AND*** lower N% «means higher cost of transportation per unit of nitrogen»

OR

«cost» increases ***AND*** inefficient/too much/about half mass not nitrogen

Accept other reasonable explanations.

*Do **not** accept answers referring to safety/explosions.*

[1 mark]

b.

	Electron geometry	Molecular geometry
Nitrogen	tetrahedral ✓	trigonal pyramidal ✓
Carbon	trigonal planar ✓	trigonal planar

Note: Urea's structure is more complex than that predicted from VSEPR theory.

[3 marks]

c. n(KNCO) «= $0.0500 \text{ dm}^3 \times 0.100 \text{ mol dm}^{-3}$» = 5.00×10^{-3} «mol»

«mass of urea = $5.00 \times 10^{-3} \text{ mol} \times 60.07 \text{ g mol}^{-1}$» = 0.300 «g»

*Award **[2]** for correct final answer.*

[2 marks]

d.i. $K_c = \frac{[(H_2N)_2CO]\times[H_2O]}{[NH_3]^2\times[CO_2]}$

[1 mark]

d.ii. «K_c» decreases ***AND*** reaction is exothermic

OR

«K_c» decreases ***AND*** ΔH is negative

OR

«K_c» decreases ***AND*** reverse/endothermic reaction is favoured

[1 mark]

d.iii. ln K « = $\frac{-\Delta G^{\ominus}}{RT} = \frac{-50\times10^3\ \mathrm{J}}{8.31\ \mathrm{J\ K^{-1}\ mol^{-1}}\times298\ \mathrm{K}}$ » = –20

«K_c =» 2×10^{-9}

OR

1.69×10^{-9}

OR

10^{-9}

Accept range of 20-20.2 for M1.

*Award **[2]** for correct final answer.*

[2 marks]

e.i. *Any one of:*

urea has greater molar mass

urea has greater electron density/greater London/dispersion

urea has more hydrogen bonding

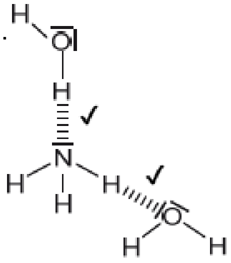
urea is more polar/has greater dipole moment

Accept “urea has larger size/greater van der Waals forces”.

*Do **not** accept “urea has greater intermolecular forces/IMF”.*

[1 mark]

e.ii.



*Award **[1]** for each correct interaction.*

*If lone pairs are shown on N or O, then the lone pair on N or one of the lone pairs on O **MUST** be involved in the H-bond.*

Penalize solid line to represent H-bonding only once.

[2 marks]

f. $2(H_2N)_2CO(s) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g) + 2N_2(g)$

correct coefficients on LHS

correct coefficients on RHS

Accept $(H_2N)_2CO(s) + \frac{3}{2}O_2(g) \rightarrow 2H_2O(l) + CO_2(g) + N_2(g)$.

Accept any correct ratio.

[2 marks]

g. «$V = \frac{0.600\text{ g}}{60.07\text{ g mol}^{-1}} \times 22700\text{ cm}^3\text{ mol}^{-1}$ =» 227 «cm^3»

[1 mark]

h. lone/non-bonding electron pairs «on nitrogen/oxygen/ligand» given to/shared with metal ion

co-ordinate/dative/covalent bonds

[2 marks]

i. lone pairs on nitrogen atoms can be donated to/shared with C–N bond

OR

C–N bond partial double bond character

OR

delocalization «of electrons occurs across molecule»

OR

slight positive charge on C due to C=O polarity reduces C–N bond length

[1 mark]

j. *60*: $CON_2H_4^+$

44: $CONH_2^+$

Accept "molecular ion".

[2 marks]

k. *3450 cm^{-1}:* N–H

1700 cm^{-1}: C=O

*Do **not** accept "O–H" for 3450 cm^{-1}.*

[2 marks]

l.i. 1

[2 marks]

l.ii. singlet

Accept "no splitting".

[1 mark]

l.iii. acts as internal standard

OR

acts as reference point

one strong signal

OR

12 H atoms in same environment

OR

signal is well away from other absorptions

Accept "inert" or "readily removed" or "non-toxic" for M1.

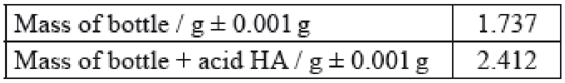
[2 marks]

Examiners report

a.i. [N/A]
a.ii. [N/A]
b. [N/A]
c. [N/A]
d.i. [N/A]
d.ii. [N/A]
d.iii. [N/A]
e.i. [N/A]
e.ii. [N/A]
f. [N/A]
g. [N/A]
h. [N/A]
i. [N/A]
j. [N/A]
k. [N/A]
l.i. [N/A]
l.ii. [N/A]
l.iii. [N/A]

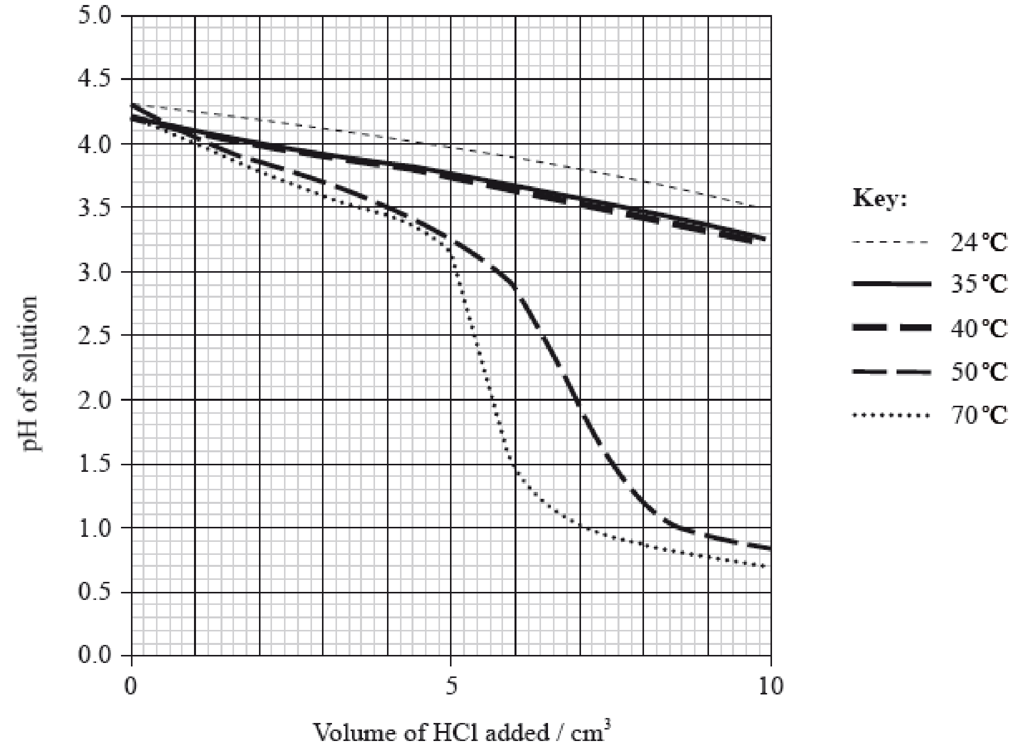
A student decided to determine the molecular mass of a solid monoprotic acid, HA, by titrating a solution of a known mass of the acid.

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 $20.0\ \mathrm{cm}^3$ 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 $10\ \mathrm{cm}^3$ 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]

Markscheme

d. $\left(\frac{\mathrm{M}}{\text{Mass of } \mathrm{C_4H_4O}} =\right) \frac{139}{68.08} = 2;$

$C_8H_8O_2;$

*Award **[2]** for correct final answer.*

f.i. solution which resists change in pH / changes pH slightly / keeps pH constant / *OWTTE*;

when small amounts of acid or base are added;

f.ii. less effective at higher temperatures / more effective between 24 °C and 40 °C than > 40 °C;

pH changes more if the same volume of acid is added at high(er) temperature / *OWTTE*;

Examiners report

d. Errors were carried forward in the marking of (d).

f.i. The common error in defining a buffer solution in (f) (i) was to omit “small” in the addition of acid or alkali whilst in (ii) candidates needed to be more specific about the volume of acid added for full credit.

f.ii. The common error in defining a buffer solution in (f) (i) was to omit “small” in the addition of acid or alkali whilst in (ii) candidates needed to be more specific about the volume of acid added for full credit.

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, ΔH_c^Θ, 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]

Markscheme

a. *Equation:*

$\mathrm{CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH/C_2H_4 + H_2O \rightarrow C_2H_5OH}$;

Conditions:

(concentrated) sulfuric acid/$\mathrm{H_2SO_4}$;

Do not accept dilute sulfuric acid.

Accept phosphoric acid/H_3PO_4 (on pellets of silicon dioxide) (for industrial preparation).

heat / high temperature;

Do not accept warm.

Accept high pressure (for industrial preparation) for M3 only if H_3PO_4 is given for M2.

b.i. energy needed to break (1 mol of) a bond in the gaseous state/phase;

(averaged over) similar compounds;

Do not accept "similar bonds" instead of "similar compounds".

Concept of "similar" is important for M2.

b.ii. $\mathrm{CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O}$;

Bonds broken:

$347 + (5 \times 413) + 358 + 464 + (3 \times 498)/4728\ (\mathrm{kJ})/\mathrm{C–C + 5C–H + C–O + O–H + 3O{=}O}$;

Bonds made:

$(4 \times 746) + (6 \times 464) = 5768\ (\mathrm{kJ})/\mathrm{4C = O + 6O–H}$;

$\Delta H = (4728 - 5768 =) - 1040\ (\mathrm{kJ\ mol^{-1}})$ / bonds broken – bonds formed;

*Award **[4]** for correct final answer.*

*Award **[3]** for (+)1040 ($kJ\ mol^{-1}$).*

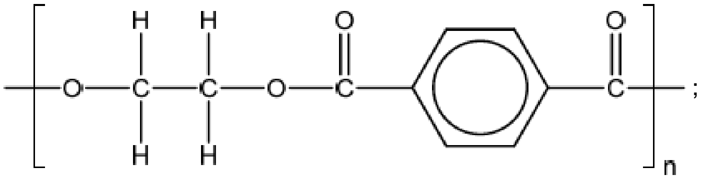
c. heat loss (to the surroundings);

d. $\mathrm{CH_3CH_2OH + CH_3CH_2COOH \rightleftharpoons CH_3CH_2OOCCH2CH_3 + H_2O}$;

ethyl propanoate;

Do not penalize if equilibrium arrow missing.

e.i. *Repeating unit*:



;

Continuation lines must be shown.

Ignore brackets and n.

Accept condensed formulas such as CH_2 and C_6H_4.

Other product:

H_2O/water;

e.ii.condensation;

f.i. $3C(s) + 3H_2(g) + O_2(g) \rightarrow CH_3CH_2COOH(l)$;

$\Delta H_f^\Theta = \sum \Delta H_c^\Theta$ (reactants) $- \sum \Delta H_c^\Theta$ (products);

Accept any suitable energy cycle.

$\sum \Delta H_c^\Theta$ (reactants) $= 3 \times (-394) + 3 \times (-286) / -2040$ (kJ mol^{-1});

$(\Delta H_f^\Theta = [3 \times (-394) + 3 \times (-286)] - (-1527) =) -513$ (kJ mol^{-1});

OR

$CH_3CH_2COOH(l) + 3.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(g)$;

$\Delta H_c^\Theta = \sum \Delta H_f^\Theta\ (products) - \sum \Delta H_f^\Theta\ (reactants)$;

$\sum \Delta H_f^\Theta$ (products) $= 3 \times (-394) + 3 \times (-286) / -2040$ (kJ mol^{-1});

$(\Delta H_f^\Theta = [3 \times (-394) + 3 \times (-286)] - (-1527) =) -513$ (kJ mol^{-1});

Ignore state symbols.

*Award **[4]** for correct final answer*.

f.ii. negative;

reduction in the number of gaseous molecules;

g. *Allotropes:*

*Any **three** allotropes for **[1]** from:*

diamond

graphite

fullerene

graphene;

Allow (carbon) nanotubes for graphene.

Accept C_{60}/C_{70}/buckminsterfullerene/bucky balls for fullerene.

Structures:

*Any three for **[3]** from:*

Diamond:

tetrahedral arrangement of (carbon) atoms/each carbon bonded to four others / sp^3 **and** 3D/covalent network structure;

Graphite:

each carbon bonded to three others (in a trigonal planar arrangement) / sp^2 **and** 2D / layers of (carbon) atoms;

Fullerene:

each (carbon) atom bonded to three others (in a trigonal arrangement) / sp^2 **and** joined in a ball/cage/sphere/connected hexagons and pentagons;

Accept "trigonal planar" for "each carbon atom bonded to three others" part in M4.

Graphene:

each carbon bonded to three others (in a trigonal arrangement) / sp^2 **and** 2D structure;

Examiners report

a. There was poor understanding of the transformation in (a). When defining the *average bond enthalpy* in (b), the notion of “gaseous” was frequently omitted and very few mentioned the bonds being in similar compounds. In the calculation, many omitted the C–C bond and many did not work from a properly balanced equation which led to disaster. Nearly every candidate attempting this question was able to suggest “heat loss”. In (d) the usual errors were made; the name was the wrong way round, water was missing from the equation and wrong products (such as pentanoic acid) were suggested. In (e) (i) the diagrams were poor but water was usually given correctly. Most gave condensation as the type of polymerization. The key to gaining marks in questions such as (f) (i) is to start with a balanced equation, [1 mark], and then set the calculation out correctly and tidily. Part marks cannot be given if the examiner cannot follow what the candidate is doing. Many correctly gave “negative” in (ii) but the explanations lacked clarity. Most gained a mark in (g) for knowing three allotropes but the description of structures was poorly done. The [4] (marks) for this part gives some idea of the amount of detail expected.

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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]

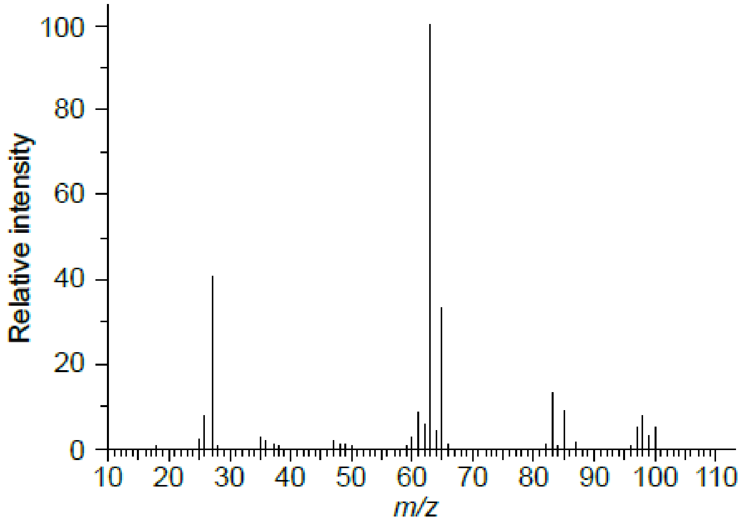
c.i. One possible product, **X**, of the reaction of ethane with chlorine has the following composition by mass: [2]

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

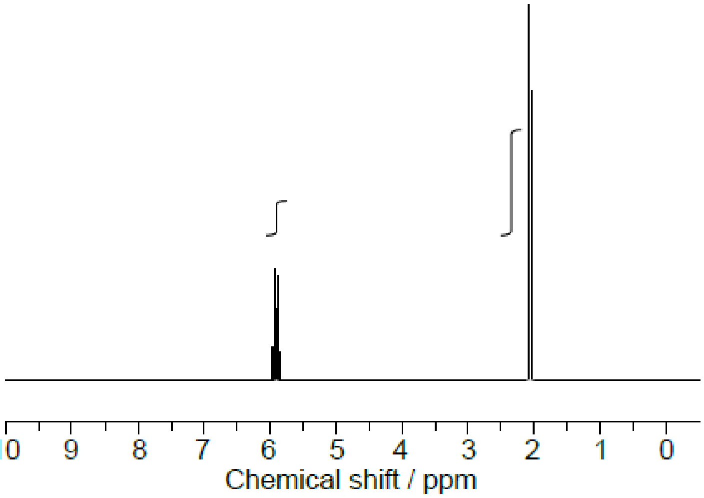
Determine the empirical formula of the product.

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]

Markscheme

a. substitution ***AND*** «free-»radical

OR

substitution ***AND*** chain

Award [1] for "«free-»radical substitution" or "S_R" written anywhere in the answer.

[1 mark]

b.i. *Two propagation steps:*

$$C_2H_6 + \bullet Cl \rightarrow C_2H_5 \bullet + HCl$$

$$C_2H_5 \bullet + Cl_2 \rightarrow C_2H_5Cl + \bullet Cl$$

One termination step:

$C_2H_5\bullet + C_2H_5\bullet \rightarrow C_4H_{10}$

OR

$C_2H_5\bullet + \bullet Cl \rightarrow C_2H_5Cl$

OR

$\bullet Cl + \bullet Cl \rightarrow Cl_2$

Accept radical without ● if consistent throughout.

Allow ECF for incorrect radicals produced in propagation step for M3.

[3 marks]

b.ii. triplet ***AND*** quartet

[1 mark]

b.iii. chemical shift/signal outside range of common chemical shift/signal

strong signal/12/all H atoms in same environment
OR
singlet/no splitting of the signal

volatile/easily separated/easily removed
OR
inert/stabl

contains three common NMR nuclei/^1H and ^{13}C and ^{29}Si

*Do **not** accept chemical shift = 0.*

[2 marks]

c.i. $C = \frac{24.27}{12.01} = 2.021$ ***AND*** $H = \frac{4.08}{1.01} = 4.04$ ***AND*** $Cl = \frac{71.65}{35.45} = 2.021$

«hence» CH_2Cl

Accept $\frac{24.27}{12.01} : \frac{4.08}{1.01} : \frac{71.65}{35.45}$.

*Do **not** accept $C_2H_4Cl_2$.*

Award [2] for correct final answer.

[2 marks]

c.ii. molecular ion peak(s) «about» *m/z* 100 ***AND*** «so» $C_2H_4Cl_2$ «isotopes of Cl»

two signals «in ^1H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
«signals in» 3:1 ratio «in ^1H NMR spectrum» ***AND*** «so» CH_3CHCl_2
OR
one doublet and one quartet «in ^1H NMR spectrum» ***AND*** «so» CH_3CHCl_2

1,1-dichloroethane

Accept "peaks" for "signals".

Allow ECF for a correct name for M3 if an incorrect chlorohydrocarbon is identified.

[3 marks]

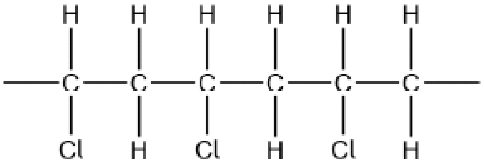
c.iii base

OR

proton acceptor

[1 mark]

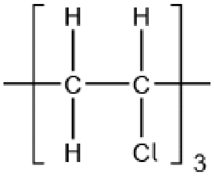
d.



Continuation bonds must be shown.

Ignore square brackets and “n”.

Accept



.

Accept other versions of the polymer, such as head to head and head to tail.

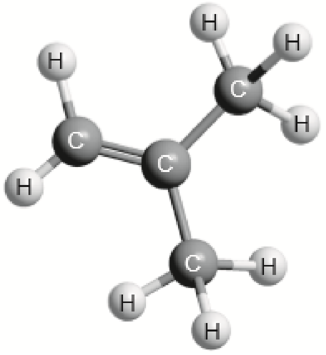
Accept condensed structure provided all C to C bonds are shown (as single).

[1 mark]

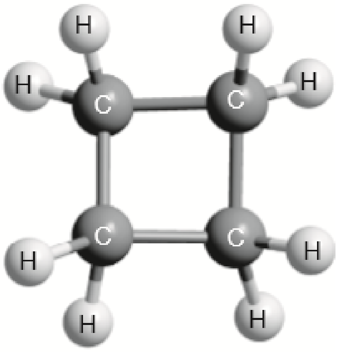
Examiners report

a. [N/A]
b.i. [N/A]
b.ii. [N/A]
b.iii. [N/A]
c.i. [N/A]
c.ii. [N/A]
c.iii. [N/A]
d. [N/A]

Compound **A** and compound **B** are hydrocarbons.



A



B

a. (i) State the term that is used to describe molecules that are related to each other in the same way as compound **A** and compound **B**. [3]

(ii) Suggest a chemical test to distinguish between compound **A** and compound **B**, giving the observation you would expect for each.

Test:

Observation with **A**:

Observation with **B**:

b. Outline how you could use the IR spectra of compounds **A** and **B** and section 26 of the data booklet to identify them. [1]

c. Two signals occur in the ^{1}H NMR spectrum of compound **A**. Deduce their expected chemical shift and their splitting pattern, using section 27 of the data booklet. [2]

Signal	**1**	**2**
Chemical shift / ppm	. . . .	. . . .
Splitting pattern	. . . .	. . . .

Markscheme

a. (i)

«structural/functional» isomer«s»

(ii)
Test:
«react with» bromine/Br_2 «in the dark»
OR
«react with» bromine water/Br_2 (aq) «in the dark»

A: from yellow/orange/brown to colourless ***AND*** *B*: colour remains/slowly decolourized

Accept other correct reagents, such as manganate(VII) or iodine solutions, and descriptions of the corresponding changes observed.

Accept "decolourized" for A and "not decolourized/unchanged" for B.
*Do **not** accept "clear/transparent" instead of "colourless".*

b. compound **A** would absorb at 1620–1680«cm^{-1}»

Accept any value in range 1620 – 1680 cm^{-1}.

c.

Signal	1/2		2/1
Chemical shift/ ppm	0.9 - 1.0	***AND***	4.5 - 6.0
Splitting pattern	singlet	***AND***	singlet

Accept 0.9 to 2.0 for the first signal as the C=C affects the CH_3 shift (actually 1.7).

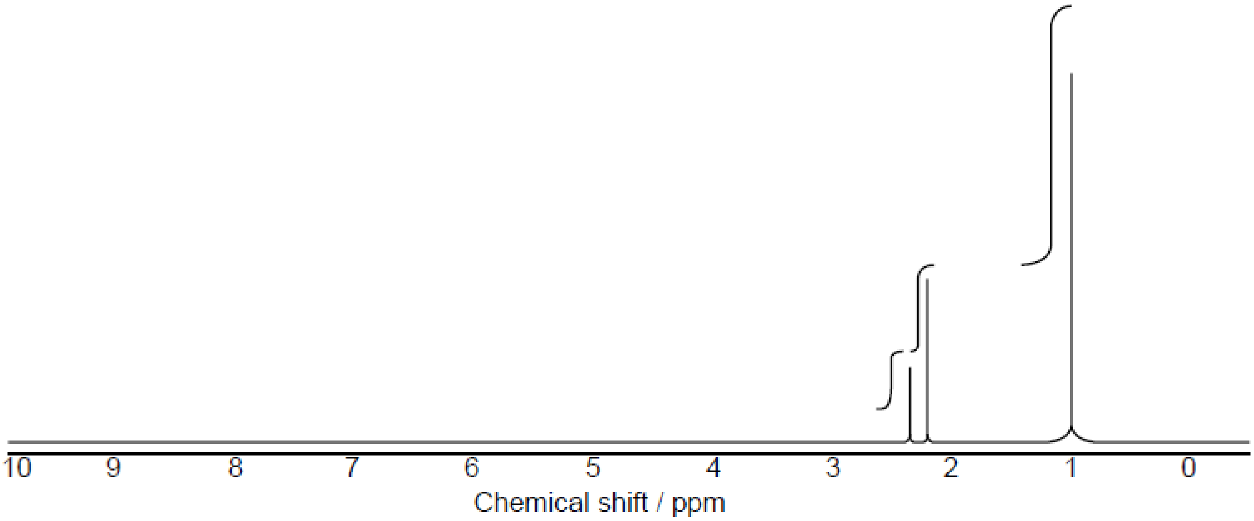
Accept "none/no splitting" for both splitting patterns

*Award **[1 max]** for the correct deduction (both shift and splitting) of signal 1 or 2.*

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]

A compound with a molecular formula $C_7H_{14}O$ produced the following high resolution ^1H NMR spectrum.



a.i. Deduce what information can be obtained from the ^1H NMR spectrum. [3]

Number of hydrogen environments:

. . . .

Ratio of hydrogen environments:

. . . .

Splitting patterns:

. . . .

a.ii. Identify the functional group that shows stretching at 1710 cm^{-1} in the infrared spectrum of this compound using section 26 of the data booklet and the ^1H NMR. [1]

a.iii. Suggest the structural formula of this compound. [2]

b.i. Bromine was added to hexane, hex-1-ene and benzene. Identify the compound(s) which will react with bromine in a well-lit laboratory. [1]

b.ii. Deduce the structural formula of the main organic product when hex-1-ene reacts with hydrogen bromide. [1]

c.i. State the reagents and the name of the mechanism for the nitration of benzene. [2]

Reagents:

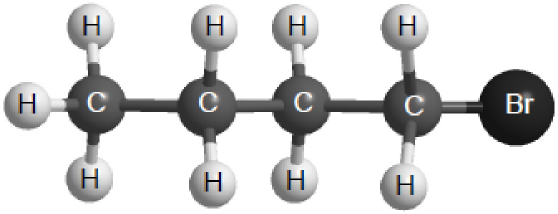
. . . .

Name of mechanism:

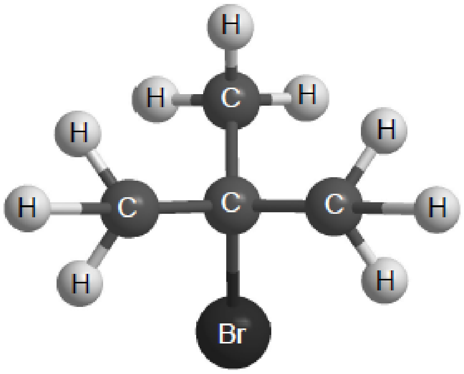
. . . .

c.ii.Outline, in terms of the bonding present, why the reaction conditions of halogenation are different for alkanes and benzene. [1]

d. Below are two isomers, A and B, with the molecular formula C_4H_9Br. [3]



A



B

Explain the mechanism of the nucleophilic substitution reaction with NaOH(aq) for the isomer that reacts almost exclusively by an S_N2 mechanism using curly arrows to represent the movement of electron pairs.

Markscheme

a.i. *Number of hydrogen environments:* 3

Ratio of hydrogen environments: 2:3:9

Splitting patterns: «all» singlets

Accept any equivalent ratios such as 9:3:2.

Accept “no splitting”.

[3 marks]

a.ii.carbonyl

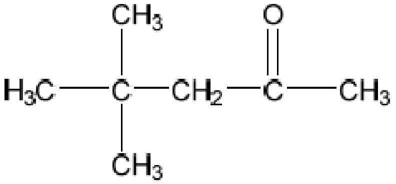
OR

C=O

Accept “ketone” but not “aldehyde”.

[1 mark]

a.iii.



Accept $(CH_3)_3CCH_2COCH_3$.

Award ***[1]*** *for any aldehyde or ketone with $C_7H_{14}O$ structural formula.*

[2 marks]

b.i. hexane ***AND*** hex-1-ene

Accept "benzene ***AND*** *hexane* ***AND*** *hex-1-ene".*

[1 mark]

b.ii. $CH_3CH_2CH_2CH_2CHBrCH_3$

Accept displayed formula but ***not*** *molecular formula.*

[1 mark]

c.i. *Reagents:* «concentrated» sulfuric acid ***AND*** «concentrated» nitric acid

Name of mechanism: electrophilic substitution

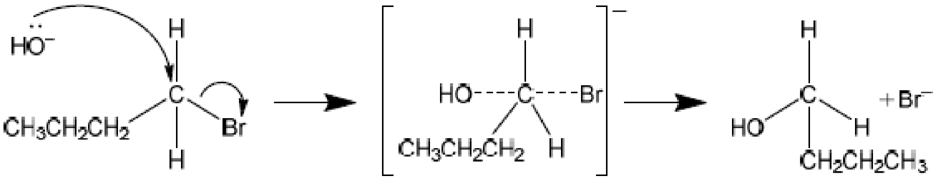
[2 marks]

c.ii. benzene has «delocalized» π bonds «that are susceptible to electrophile attack» ***AND*** alkanes do not

Do ***not*** *accept "benzene has single and double bonds".*

[1 mark]

d.



curly arrow going from lone pair/negative charge on O in ^{-}OH to C

curly arrow showing Br leaving

representation of transition state showing negative charge, square brackets and partial bonds

Accept OH^- with or without the lone pair.

Do not allow curly arrows originating on H in OH^-.

Accept curly arrows in the transition state.

Do not penalize if HO and Br are not at 180°.

Do not award M3 if OH–C bond is represented.

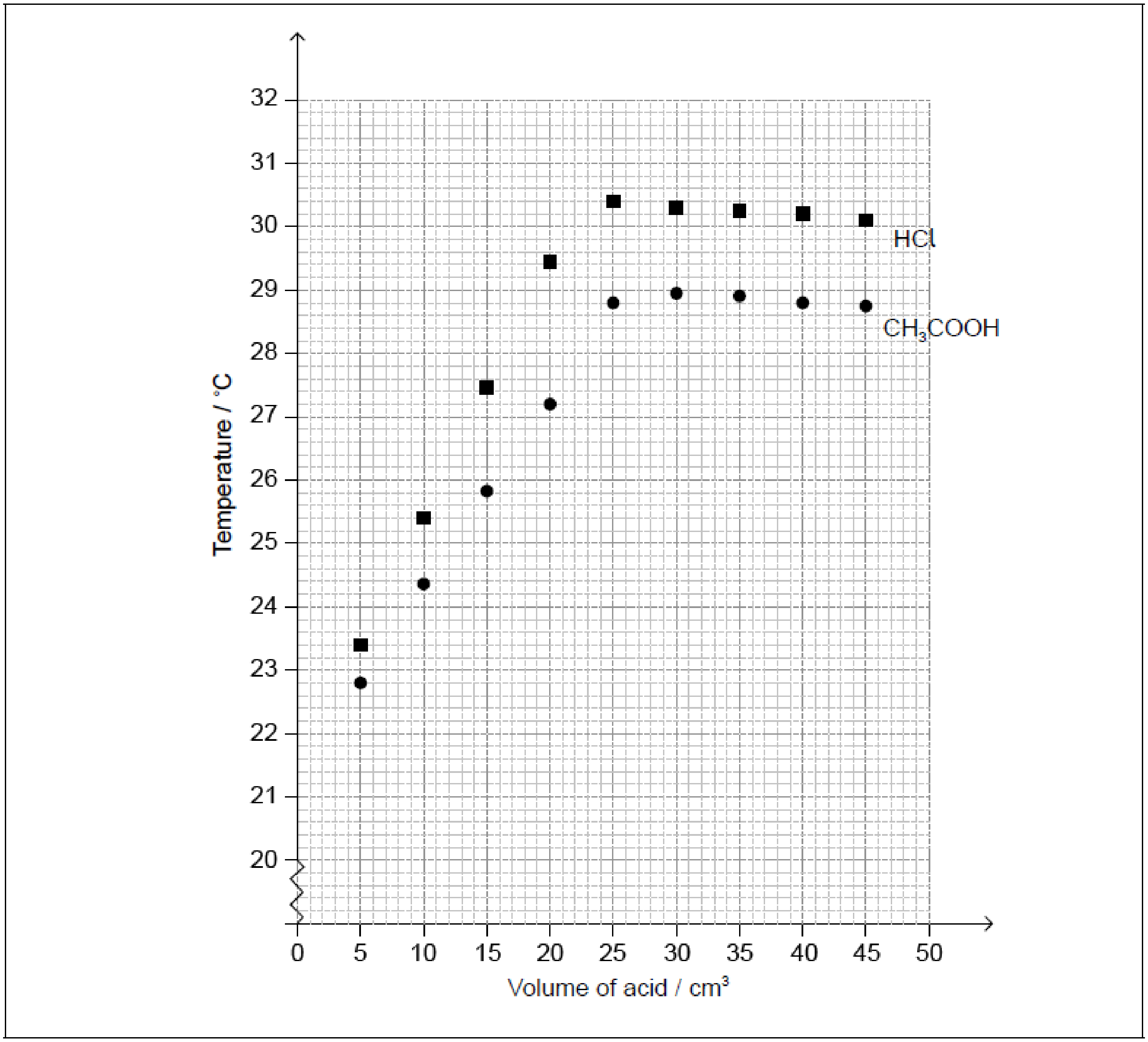
Award ***[2 max]*** *if wrong isomer is used.*

[3 marks]

Examiners report

a.i. [N/A]
a.ii. [N/A]
a.iii. [N/A]
b.i. [N/A]
b.ii. [N/A]
c.i. [N/A]
c.ii. [N/A]
d. [N/A]

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:

. . . .

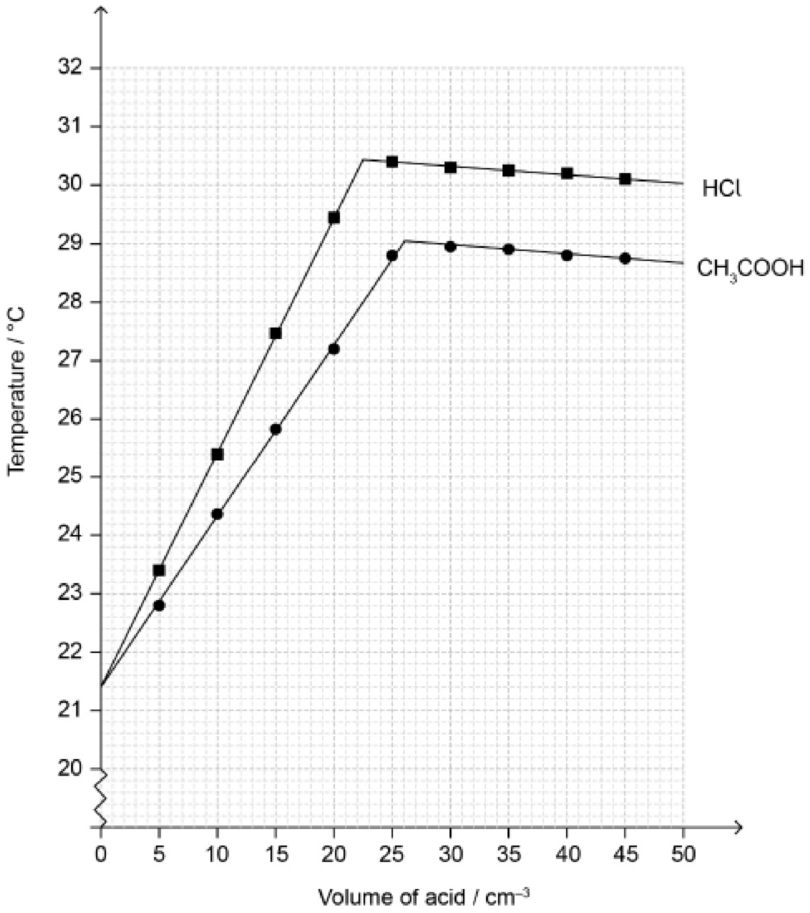
CH_3COOH:

. . . .

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

Markscheme

a.



21.4 °C

Accept values in the range of 21.2 to 21.6 °C.
Accept two different values for the two solutions from within range.

b. *HCl:* 30.4 «°C»

Accept range 30.2 to 30.6 °C.

CH_3COOH: 29.0 «°C»

Accept range 28.8 to 29.2 °C.

e. CH_3COOH is weak acid/partially ionised

energy used to ionize weak acid «before reaction with NaOH can occur»

Examiners report

a. [N/A]
b. [N/A]
e. [N/A]

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

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

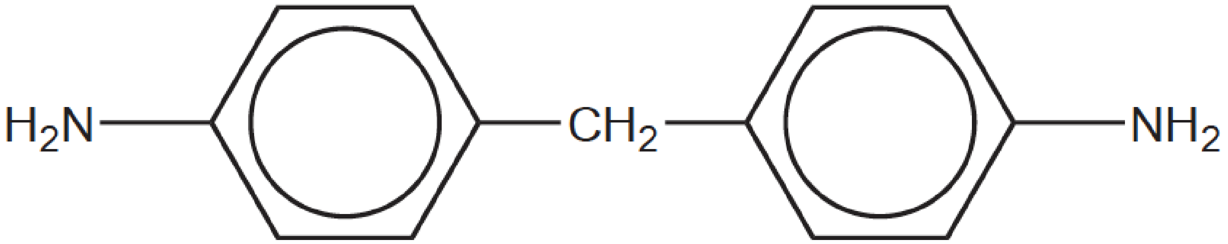
a. (i) Deduce the equilibrium constant expression, K_c, for this reaction. [8]

(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 $-220.1 kJmol^{-1}$. 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

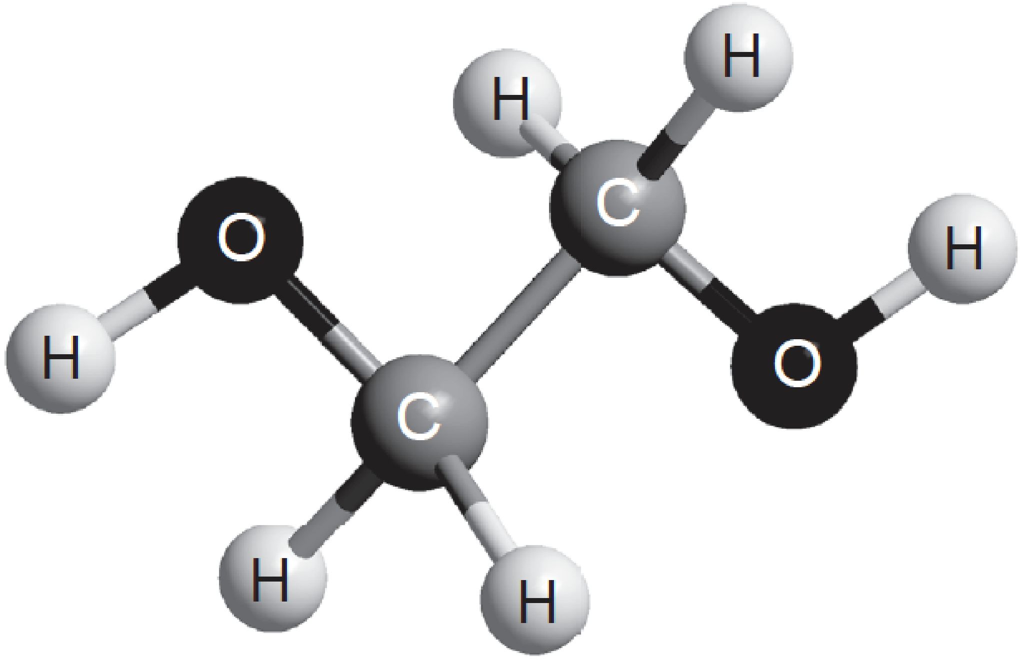
(i) Classify diamine **X** as a primary, secondary or tertiary amine.

(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.

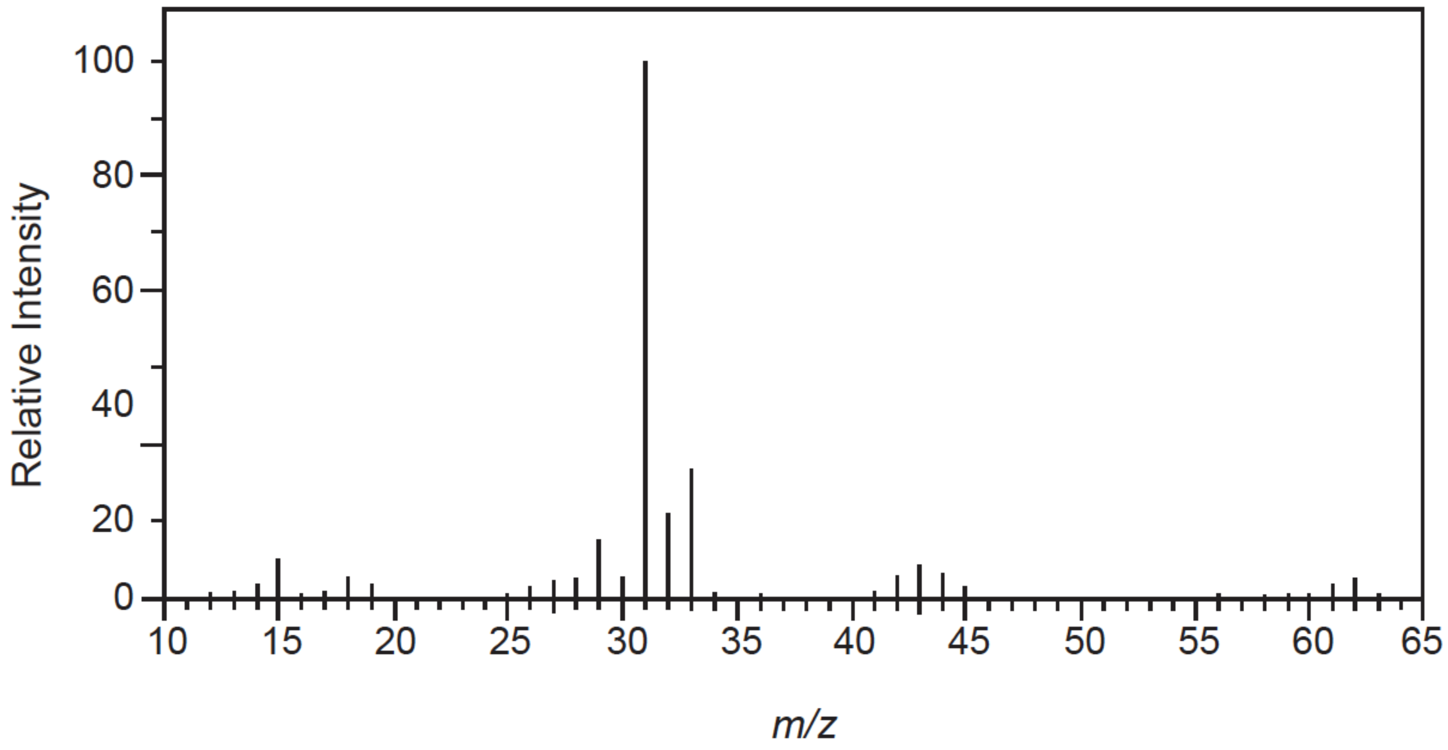
Name:

Class:

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

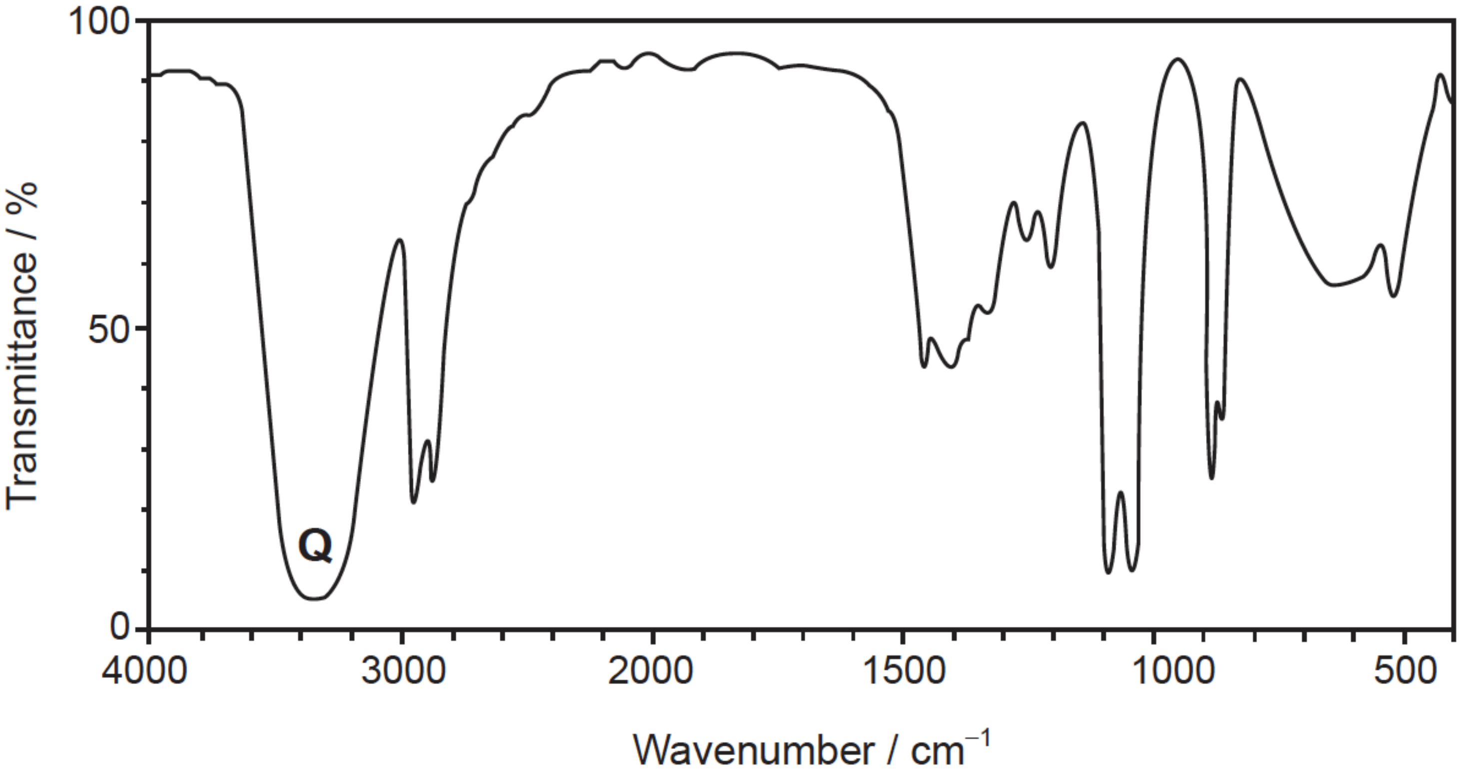
The mass spectrum and infrared (IR) spectrum of compound **Z** are shown below:

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]

Markscheme

a. (i)

$\ll K_C = \gg \frac{[COCl_2]}{[CO][Cl_2]}$

(ii)
T«= 600 + 273» = 873K

$\Delta G^\ominus = -8.31 \times 873 \times \ln(0.200)$
OR
$\Delta G^\ominus$ = « + » 11676 «J»
$\Delta G^\ominus$ = « + » 11.7 «kJ»

Accept 11.5 to 12.0.
Award final mark only if correct sig fig.
*Award **[3]** for correct final answer.*

(iii)
$\Delta H^\ominus = -220.1 - (-110.5)$
$\Delta H^\ominus = -109.6$ «kJ»

*Award **[2]** for correct final answer.*
*Award **[1]** for –330.6, or +109.6 «kJ».*

(iv)

$\Delta G^{\ominus} = -109.6 - (298 \times \Delta S^{\ominus}) = +11.7$ «kJ»

$\Delta S^{\ominus}$«$\frac{(11.7+109.6)\times 10^3}{298}$»$= -407$ «JK^{-1}»

*Award **[2]** for correct final answer.*
*Award **[2]** for –470 «JK^{-1}» (result from given values).*
Do not penalize wrong value for T if already done in (a)(ii).
*Award **[1 max]** for –0.407 «$kJ\ K^{-1}$».*
*Award **[1 max]** for –138.9 «$J\ K^{-1}$».*

b. (i)

primary

(ii)

ALTERNATIVE 1:
«heat with» tin/Sn ***AND*** hydrochloric acid/HCl
aqueous alkali/OH^-(aq)

ALTERNATIVE 2:

hydrogen/H_2

nickel/Ni «catalyst»

Accept specific equations having correct reactants.
*Do **not** accept LiAlH4 or NaBH4.*
Accept Pt or Pd catalyst.

Accept equations having correct reactants.

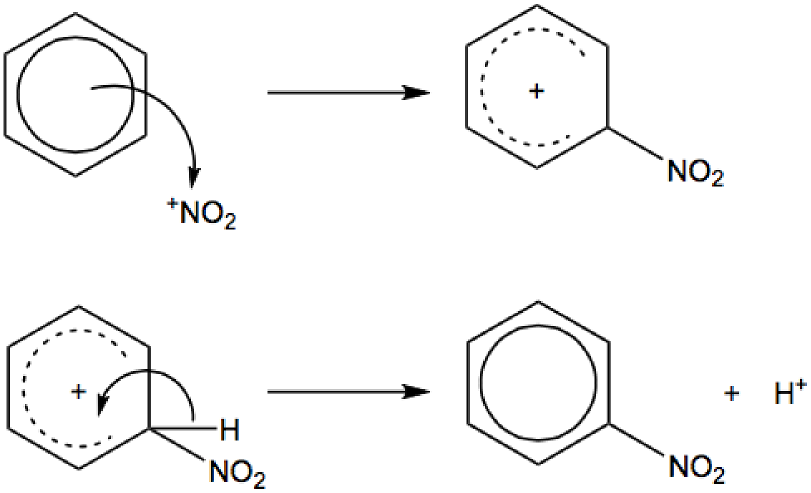
(iii)

$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + 2HSO_4^- + H_3O^+$

Accept: $HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$ *Accept* $HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$.

Accept equivalent two step reactions in which sulfuric acid first behaves as a strong acid and protonates the nitric acid, before behaving as a dehydrating agent removing water from it.

(iv)



curly arrow going from benzene ring to N of $^+NO_2/NO_2^+$

carbocation with correct formula and positive charge on ring

curly arrow going from C–H bond to benzene ring of cation formation of organic product nitrobenzene ***AND*** H^+

Accept mechanism with corresponding Kekulé structures.

*Do **not** accept a circle in M2 or M3. Accept first arrow starting either inside the circle or on the circle.*

M2 may be awarded from correct diagram for M3.

M4: Accept $C_6H_5NO_2 + H_2SO_4$ if HSO_4^- used in M3.

c. (i)

Name: ethane-1,2-diol

Class: alcohol«s»

Accept ethan-1,2-diol / 1,2-ethanediol.

*Do **not** accept "diol" for Class.*

(ii)
two ***AND*** two hydrogen environments in the molecule
OR
two ***AND*** both CH_2 and OH present

(iii)
$^+CH_2OH$

Accept CH_3O^+.

Accept $[\bullet CH_2OH]^+$ and $[\bullet CH_3O]^+$.

Do not accept answers in which the charge is missing.

(iv)
oxygen-hydrogen «bond»/O–H «in hydroxyl»

d. $K_b \approx \frac{[OH^-]^2}{[C_6H_5NH_2]} = 10^{-9.13}/7.413 \times 10^{-10}$

$[OH^-] = \sqrt{0.0100 \times 10^{-9.13}} = 2.72 \times 10^{-6}$

$[H^+] = \frac{1\times10^{-14}}{2.72\times10^{-6}} = 3.67 \times 10^{-9}$

OR

pOH = 5.57

pH = –log $[H^+]$ = 8.44

Accept other approaches to the calculation.
*Award **[4]** for correct final answer.*
Accept any answer from 8.4 to 8.5.

Examiners report

a. [N/A]
b. [N/A]
c. [N/A]
d. [N/A]