HL Paper 2

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

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

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

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

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

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

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

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

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

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

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

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

Hydrazine, N_2H_4, is a valuable rocket fuel.

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

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

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

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

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

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

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

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

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

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

(iv) Calculate $\Delta S^\ominus$ for the reaction using the data below and comment on its magnitude.

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

(v) Calculate $\Delta G^\ominus$ for the reaction at 298 K.

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

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

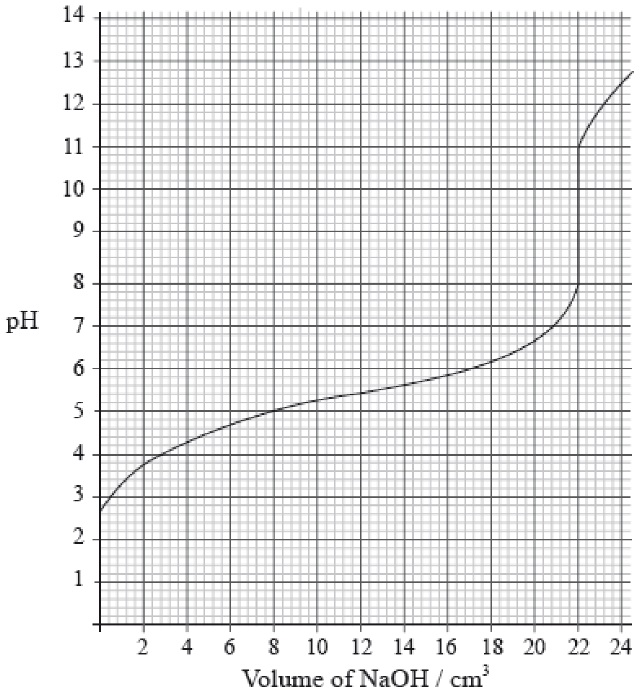
$$N_2H_4(aq) + 2HCl(aq) \rightarrow N_2H_6^{2+}(aq) + 2Cl^-(aq)$$

(i) Identify the type of reaction that occurs.

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

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

A 25.0 cm^3 solution of a weak monoprotic acid, HA(aq), is titrated with $0.155 \text{ mol dm}^{-3}$ sodium hydroxide, NaOH(aq), and the following graph is obtained.



0.100 mol of ammonia, NH_3, was dissolved in water to make $1.00\ dm^3$ of solution. This solution has a hydroxide ion concentration of $1.28 \times 10^{-3}\ mol\,dm^{-3}$.

a.i. Determine the pH at the equivalence point. [1]

a.ii. Explain, using an equation, why the equivalence point is not at $pH = 7$. [3]

a.iii. Calculate the concentration of the weak acid before the addition of any NaOH(aq). [2]

a.iv. Estimate, using data from the graph, the dissociation constant, K_a, of the weak acid, HA, showing your working. [3]

a.v. Suggest an appropriate indicator for this titration. [1]

b. Describe qualitatively the action of an acid-base indicator. [3]

c.i. Explain what is meant by the term *buffer solution*. [2]

c.ii. Calculate the pH of a solution prepared by mixing $50.0\ cm^3$ of $0.200\ mol\,dm^{-3}\ CH_3COOH(aq)$ and $50.0\ cm^3$ of , $0.100\ mol\,dm^{-3}\ NaOH(aq)$ showing your working. [3]

e.i. Determine the pH of the solution. [2]

e.ii. Calculate the base dissociation constant, K_b, for ammonia. [3]

Hypochlorous acid, HOCl(aq), is an example of a weak acid.

A household bleach contains sodium hypochlorite, NaOCl(aq), at a concentration of $0.705\ mol\,dm^{-3}$. The hypochlorite ion, $OCl^-(aq)$ is a weak base.

$$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$$

a. State the expression for the ionic product constant of water, K_w. [1]

b.i. The pK_a value of HOCl(aq) is 7.52. Determine the K_b value of $OCl^-(aq)$ assuming a temperature of 298 K. [1]

b.ii. Determine the concentration of $OH^-(aq)$, in $mol\,dm^{-3}$, at equilibrium and state **one** assumption made in arriving at your answer other than a temperature of 298 K. [3]

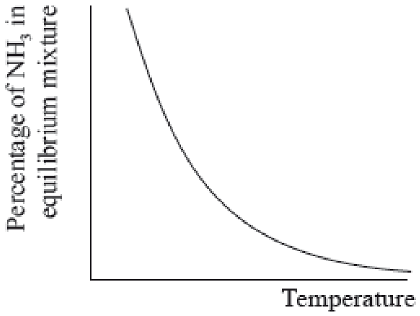
b.iii. Calculate the pH of the bleach. [2]

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

The equation for the Haber process is given below.

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Water is an important substance that is abundant on the Earth’s surface.

Buffer solutions resist small changes in pH. A phosphate buffer can be made by dissolving NaH_2PO_4 and Na_2HPO_4 in water, in which NaH_2PO_4 produces the acidic ion and Na_2HPO_4 produces the conjugate base ion.

A $0.10\ \text{mol dm}^{-3}$ ammonia solution is placed in a flask and titrated with a $0.10\ \text{mol dm}^{-3}$ hydrochloric acid solution.

a. (i) State the expression for the ionic product constant of water, K_w. [7]

(ii) Explain why even a very acidic aqueous solution still has some OH^- ions present in it.

(iii) State and explain the effect of increasing temperature on the value of K_w given that the ionization of water is an endothermic process.

(iv) State and explain the effect of increasing temperature on the pH of water.

b. (i) Deduce the acid and conjugate base ions that make up the phosphate buffer and state the ionic equation that represents the phosphate buffer. [7]

(ii) Describe how the phosphate buffer minimizes the effect of the addition of a strong base, $OH^-(aq)$, to the buffer. Illustrate your answer with an ionic equation.

(iii) Describe how the phosphate buffer minimizes the effect of the addition of a strong acid, $H^+(aq)$, to the buffer. Illustrate your answer with an ionic equation.

c. (i) Explain why the pH of the ammonia solution is less than 13. [11]

(ii) Estimate the pH at the equivalence point for the titration of hydrochloric acid with ammonia and explain your reasoning.

(iii) State the equation for the reaction of ammonia with water and write the K_b expression for $NH_3(aq)$.

(iv) When half the ammonia has been neutralized (the half-equivalence point), the pH of the solution is 9.25. Deduce the relationship between $[NH_3]$ and $[NH_4^+]$ at the half-equivalence point.

(v) Determine pK_b and K_b for ammonia based on the pH at the half-equivalence point.

(vi) Describe the significance of the half-equivalence point in terms of its effectiveness as a buffer.

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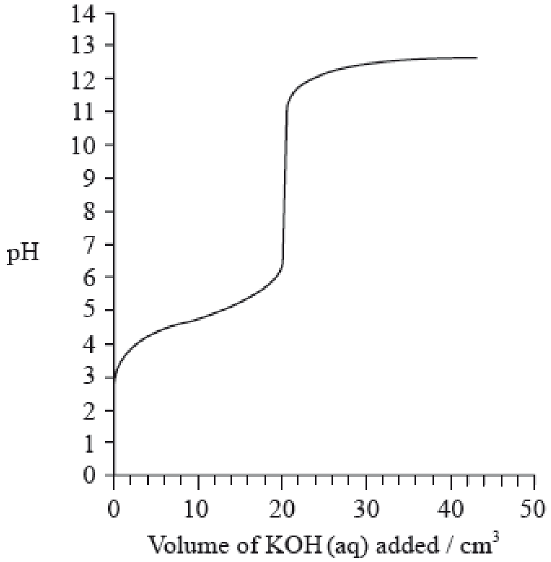
a.i. Define the terms *acid* and *base* according to the Brønsted-Lowry theory. Distinguish between a weak base and a strong base. State **one** example of a weak base. [3]

a.ii. Weak acids in the environment may cause damage. Identify a weak acid in the environment **and** outline **one** of its effects. [2]

a.iii. The graph below indicates the pH change during the titration of $20.0\ \text{cm}^3$ of $0.100\ \text{mol dm}^{-3}$ of $CH_3COOH(aq)$ with $0.100\ \text{mol dm}^{-3}\ KOH(aq)$. From the graph, identify the volume of KOH(aq) and the pH at the equivalence point. [2]



a.iv. Explain how the graph could be used to determine the pK_a of ethanoic acid **and** determine the pK_a value for these data. [2]

a.v. Sketch a graph, similar to the graph on the previous page, to indicate the change in pH during a titration of $25.0\ cm^3$ of $0.100\ mol\ dm^{-3}\ HNO_3(aq)$ with $0.100\ mol\ dm^{-3}$ KOH(aq). On your graph, clearly indicate the starting pH value, the equivalence point, the pH at the equivalence point and the final pH reached. [4]

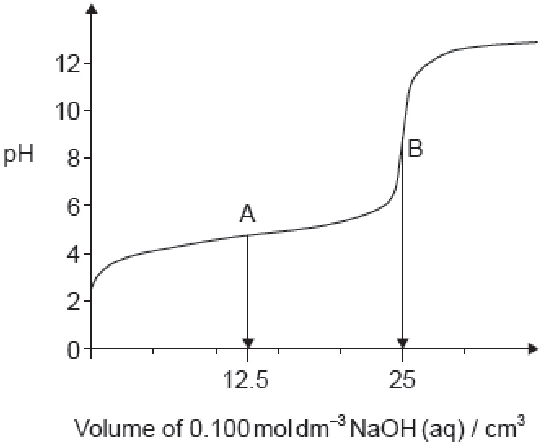
b.i. Describe how an indicator works. [3]

b.ii. Using Table 16 of the Data Booklet, identify the most appropriate indicator for the titration of ethanoic acid with potassium hydroxide. Explain your choice. [2]

d. Determine the pH of the solution resulting when $100\ cm^3$ of $0.50\ mol\ dm^{-3}\ HCl(aq)$ is mixed with $200\ cm^3$ of $0.10\ mol\ dm^{-3}\ NaOH(aq)$. [5]

Graphing is an important tool in the study of rates of chemical reactions.

d.i. The graph represents the titration of 25.00 cm^3 of 0.100 mol dm^{-3} aqueous ethanoic acid with 0.100 mol dm^{-3} aqueous sodium hydroxide. [2]



Deduce the **major** species, other than water and sodium ions, present at points A and B during the titration.

A:

B:

d.ii. Calculate the pH of 0.100 mol dm^{-3} aqueous ethanoic acid. [2]

$K_a = 1.74 \times 10^{-5}$

d.iii. Outline, using an equation, why sodium ethanoate is basic. [1]

d.iv. Predict whether the pH of an aqueous solution of ammonium chloride will be greater than, equal to or less than 7 at 298 K. [1]

e.i. Formulate the equation for the reaction of nitrogen dioxide, NO_2, with water to form two acids. [1]

e.ii. Formulate the equation for the reaction of one of the acids produced in (e)(i) with calcium carbonate. [1]

Limescale, $CaCO_3(s)$, can be removed from water kettles by using vinegar, a dilute solution of ethanoic acid, $CH_3COOH(aq)$.

a. Predict, giving a reason, a difference between the reactions of the same concentrations of hydrochloric acid and ethanoic acid with samples of calcium carbonate. [2]

b. Dissolved carbon dioxide causes unpolluted rain to have a pH of approximately 5, but other dissolved gases can result in a much lower pH. State one environmental effect of acid rain. [1]

c. Write an equation to show ammonia, NH_3, acting as a Brønsted–Lowry base and a different equation to show it acting as a Lewis base. [2]

Brønsted–Lowry base:

Lewis base:

d. Determine the pH of 0.010 mol dm^{-3} 2,2-dimethylpropanoic acid solution. [2]

K_a (2,2-dimethylpropanoic acid) = 9.333×10^{-6}

e. Explain, using appropriate equations, how a suitably concentrated solution formed by the partial neutralization of 2,2-dimethylpropanoic acid with sodium hydroxide acts as a buffer solution. [2]

Acid–base chemistry can play a major role in chemical and biological processes.

White vinegar, which contains ethanoic acid, CH_3COOH, can be used as a cleaning agent to dissolve mineral deposits from coffee machines.

Buffer solutions play a pivotal role in solution chemistry.

Acid–base indicators are often organic dyes.

a. Ammonia, NH_3, can be used to clean ovens. The concentration of hydroxide ions, $OH^-(aq)$, in a solution of ammonia is $3.98 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}$. Calculate its pH, correct to **one** decimal place, at 298 K. [2]

b.i. Define an *acid* according to the Brønsted–Lowry theory and the Lewis theory. [2]

Brønsted–Lowry theory:

Lewis theory:

b.ii. Ethanoic acid is an example of a weak acid. Distinguish between a *strong acid* and a *weak acid* in terms of the extent of dissociation. [1]

c.i. State whether the following mixtures, in the appropriate molar ratios, can be classified as buffer solutions. Show your answer by stating **yes** or **no** in the table below. [1]

Mixture	**Buffer**
$HCOOH$ and $HCOO^-K^+$	
HCl and excess NH_3	

d.i. Describe qualitatively the action of an acid–base indicator. [3]

d.ii. Using Table 16 of the Data Booklet, identify the most appropriate indicator for the titration of ethanoic acid with sodium hydroxide. Explain your choice. [2]

d.iii. $150\ \mathrm{cm^3}$ of $5.00 \times 10^{-1}\ \mathrm{mol\,dm^{-3}}$ HCl (aq) is mixed with $300\ \mathrm{cm^3}$ of $2.03 \times 10^{-1}\ \mathrm{mol\,dm^{-3}}$ NaOH(aq). Determine the pH of the solution, correct to **two** decimal places. [4]

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]

Antimony, Sb, forms a fluoride, $\mathrm{SbF_5}$.

The equilibrium that occurs when antimony(V) fluoride is dissolved in liquid hydrogen fluoride can be represented by the equation below.

$$\mathrm{SbF_5(s) + 2HF(l) \rightleftharpoons SbF_6^-(sol) + H_2F^+(sol)}$$

Outline how the following factors account for the fact that HCl is a strong acid and HF is a weak acid.

Some students were provided with a $0.100\ \mathrm{mol\,dm^{-3}}$ solution of a monobasic acid, HQ, and given the problem of determining whether HQ was a weak acid or a strong acid.

The second problem set for the students was to determine the acid dissociation constant, K_a, of the acid HQ and its $\mathrm{p}K_\mathrm{a}$.

a. State the element that you would expect to have chemical properties most similar to those of antimony. [1]

b.i. Describe the relationship between $\mathrm{SbF_5}$ and $\mathrm{SbF_6^-}$ in terms of the Lewis theory of acids. [2]

b.ii. Explain the behaviour of HF in terms of the Brønsted–Lowry theory of acids. [2]

c.i. The strength of the hydrogen–halogen bond. [1]

c.ii. The interaction between an undissociated hydrogen halide molecule and a water molecule. [1]

d.i. Neelu and Charles decided to solve the problem by determining the volume of $0.100\ \mathrm{mol\,dm^{-3}}$ sodium hydroxide solution needed to neutralize $25.0\ \mathrm{cm^3}$ of the acid. Outline whether this was a good choice. [2]

d.ii. Identify **one** indicator that could be used when titrating aqueous sodium hydroxide with both a strong acid and a weak acid, and outline the reason for your choice. [2]

Indicator:

Reason:

d.iii. Neelu and Charles decided to compare the volume of sodium hydroxide solution needed with those required by known $0.100\ \mathrm{mol\,dm^{-3}}$ strong and weak acids. Unfortunately they chose sulfuric acid as the strong acid. Outline why this was an unsuitable choice. [1]

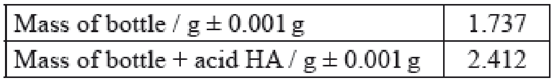
d.iv. Francisco and Shamiso decided to measure the pH of the initial solution, HQ, and they found that its pH was 3.7. Deduce, giving a reason, the strength (weak or strong) of the acid HQ. [2]

e.i. Explain how the $\mathrm{p}K_\mathrm{a}$ could be determined from a graph of pH against the volume of $0.100\ \mathrm{mol\,dm^{-3}}$ sodium hydroxide added. [2]

e.ii. Francisco and Shamiso found that the pH of the initial $0.100\ \mathrm{mol\,dm^{-3}}$ solution was 3.7. However, this reading was inaccurate because they forgot to wash the pH probe. Calculate the $\mathrm{p}K_\mathrm{a}$ of HQ using the reading they obtained. [4]

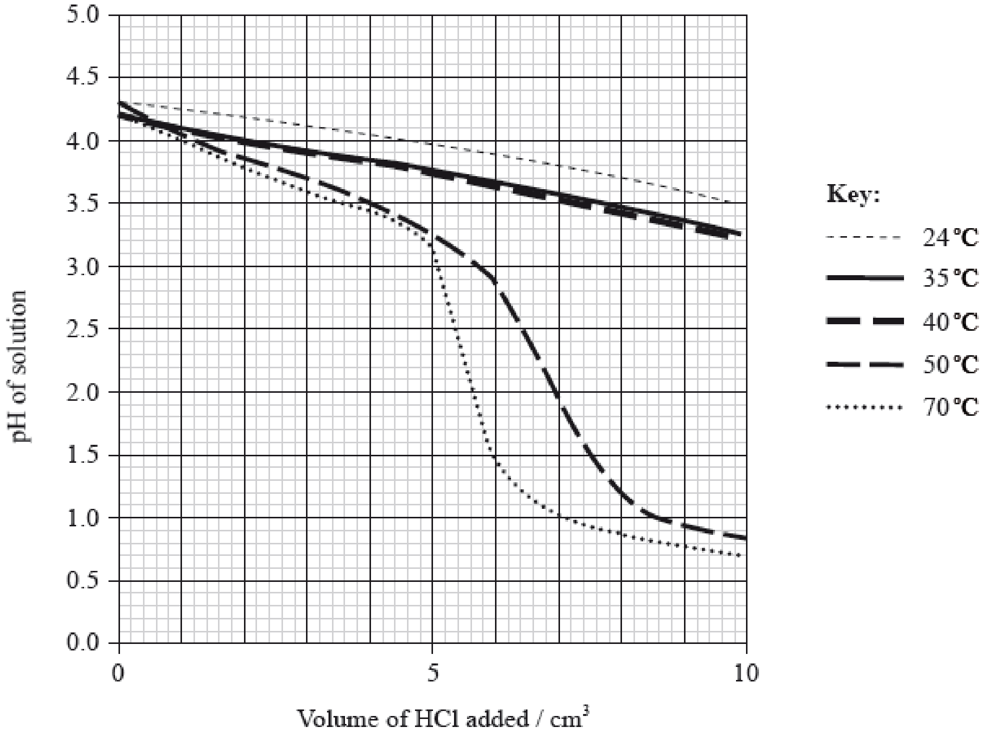
A student decided to determine the molecular mass of a solid monoprotic acid, HA, by titrating a solution of a known mass of the acid.

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]

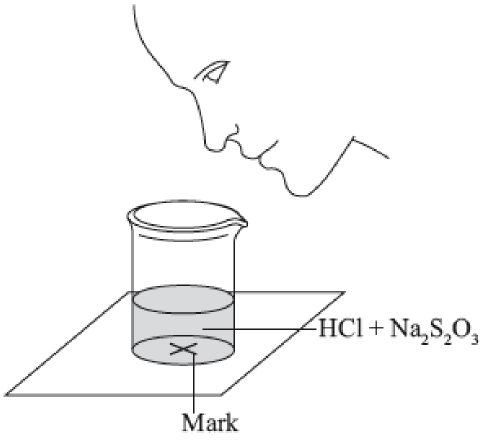
f.i. State what is meant by a *buffer solution*. [2]

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

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

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

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



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

One proposed mechanism for this reaction is:

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

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

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

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

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

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

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

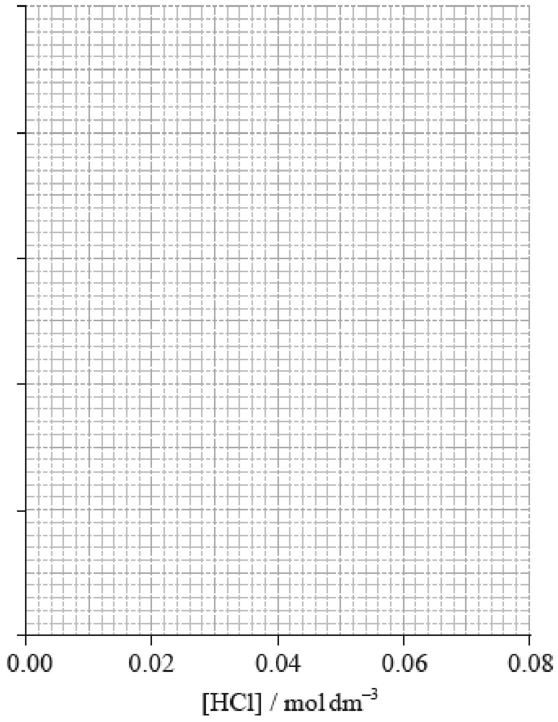
(iii) If the reaction were first order with respect to the thiosulfate ion, predict the time it would take for the mark on the paper to be obscured when the concentration of sodium thiosulfate solution is halved.

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

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

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

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



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

c. (i) Sketch and label, indicating an approximate activation energy, the Maxwell–Boltzmann energy distribution curves for two temperatures, T_1 and $T2$ $(T_2 > T_1)$, at which the rate of reaction would be significantly different. [6]

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

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

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

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

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

$$\text{SO}_2(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$$

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

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

Iron tablets are often prescribed to patients. The iron in the tablets is commonly present as iron(II) sulfate, FeSO_4.

h.i. Following the experiment, the students proposed the following hypothesis: [1]

"Since sulfuric acid is a strong acid, two other strong acids such as nitric acid, HNO_3(aq) or hydrochloric acid, HCl(aq), could also be used in this experiment".

Suggest **one** problem with this hypothesis.

h.ii. The students also explored the role of sulfuric acid in everyday processes and found that sulfuric acid present in acid rain can damage buildings made of limestone. Predict the balanced chemical equation for the reaction between limestone and sulfuric acid, including state symbols. [2]

Calcium nitrate contains both covalent and ionic bonds.

Nitrogen also forms oxides, which are atmospheric pollutants.

a.i. State the formula of both ions present and the nature of the force between these ions. [2]

Ions:

Nature of force:

a.ii. State which atoms are covalently bonded. [1]

b. Bonding in the nitrate ion involves electron delocalization. Explain the meaning of electron delocalization and how it affects the ion. [2]

c.i. Outline the source of these oxides. [1]

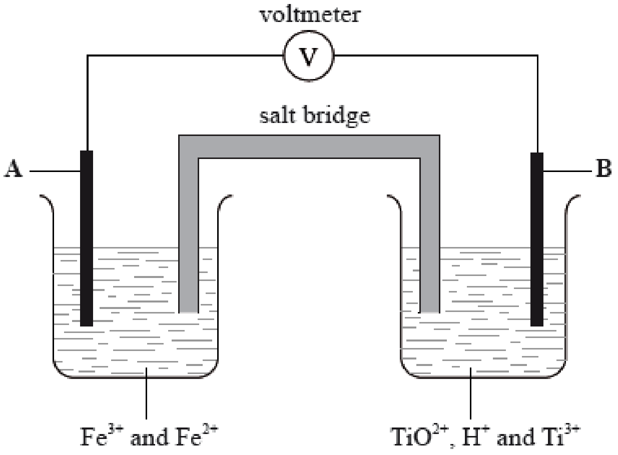
c.ii. State **one** product formed from their reaction with water. [1]

c.iii. State **one** environmental problem caused by these atmospheric pollutants. [1]

In acidic solution, ions containing titanium can react according to the half-equation below.

$$\mathrm{TiO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons Ti^{3+}(aq) + H_2O(l)} \quad E^\ominus = -0.06\ \mathrm{V}$$

In the diagram below, **A** and **B** are inert electrodes and, in the aqueous solutions, all ions have a concentration of $1\ \mathrm{mol\,dm^{-3}}$.



Sodium, silicon and sulfur are elements in period 3 of the periodic table that all form oxides.

Although carbon and silicon both belong to group 4 of the periodic table, carbon dioxide and silicon dioxide are different in many ways.

a. Define the term *standard electrode potential*, $E^\ominus$. [1]

b.i. State the initial and final oxidation numbers of titanium and hence deduce whether it is oxidized or reduced in this change. [2]

Initial oxidation number	**Final oxidation number**	**Oxidized / reduced**

b.ii. Considering the above equilibrium, predict, giving a reason, how adding more acid would affect the strength of the TiO^{2+} ion as an oxidizing agent. [2]

c. In the two experiments below, predict whether a reaction would occur and deduce an equation for any reaction that takes place. Refer to Table 14 of the Data Booklet if necessary. [3]

KI(aq) is added to a solution containing $\mathrm{Ti}^{3+}(\mathrm{aq})$ ions:

Zn (s) is added to a solution containing $\mathrm{TiO}^{2+}(\mathrm{aq})$ and $\mathrm{H}^{+}(\mathrm{aq})$ ions:

d.i. Using Table 14 of the Data Booklet, state the balanced half-equation for the reaction that occurs at electrode **A** and whether it involves oxidation or reduction. [2]

d.ii. Calculate the cell potential in V. [1]

d.iii. On the diagram above label with an arrow [1]

- the direction of electron flow in the wire
- the direction in which the positive ions flow in the salt bridge.

e.i. Compare the properties of the three oxides by completing the table below. [3]

	Na_2O	**SiO_2**	**SO_2**
Bonding type			
Standard state			
Effect on pH of water			

e.ii. Sulfur dioxide is a significant contributor to acid deposition. Identify a major, man-made source of this pollutant. [1]

e.iii. As well as the oxide above, sodium forms a peroxide that contains the peroxide ion, O_2^{2-}. Draw the Lewis (electron dot) structure of the peroxide ion. [2]

f.i. Describe the differences in the hybridization of these group 4 elements and the precise nature of the bonds that they form with the oxygen atoms. [3]

f.ii. Xenon, although a noble gas, forms an oxide, XeO_2, that has a structure related to that of SiO_2. Compare the geometry around the silicon atoms in SiO_2 with the geometry around the xenon atoms in XeO_2, using the valence shell electron pair repulsion (VSEPR) theory. [3]

Oxidation and reduction can be defined in terms of electron transfer or oxidation numbers.

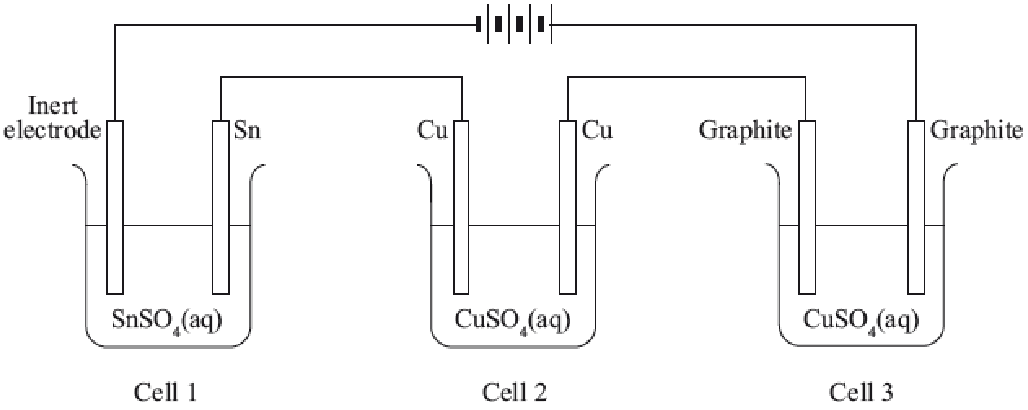
A reactivity series can be experimentally determined by adding the metals W, X, Y and Z to solutions of these metal ions. The following reactions were observed:

$$W^{2+}(aq) + X(s) \rightarrow W(s) + X^{2+}(aq)$$
$$Y(s) + W^{2+}(aq) \rightarrow Y^{2+}(aq) + W(s)$$
$$Z^{2+}(aq) + W(s) \rightarrow Z(s) + W^{2+}(aq)$$
$$Y(s) + X^{2+}(aq) \rightarrow Y^{2+}(aq) + X(s)$$

A student carries out the electrolysis of aqueous potassium iodide, KI, using inert electrodes.

Three electrolytic cells were set up in series (one cell after the other), as shown below.

All of the solutions had a concentration of 1.00 mol dm^{-3}.



a. Alcohols with the molecular formula C_4H_9OH occur as four structural isomers. Three of the isomers can be oxidized with acidified potassium dichromate solution to form compounds with the molecular formula C_4H_8O. [9]

(i) Deduce the half-equation for the oxidation of the alcohol C_4H_9OH.

(ii) Deduce the overall equation for the redox reaction.

(iii) Two of the isomers with the molecular formula C_4H_9OH can be oxidized further to form compounds with the molecular formula $C_4H_8O_2$. Deduce the structural formulas of these two isomers.

(iv) One isomer cannot be oxidized by acidified potassium dichromate solution.

Deduce its structural formula, state its name and identify it as a primary, secondary or tertiary alcohol.

Name:

Alcohol:

(v) All isomers of the alcohol C_4H_9OH undergo complete combustion. State an equation for the complete combustion of C_4H_9OH.

b. (i) Deduce the order of reactivity of these four metals, from the least to the most reactive. [6]

(ii) A voltaic cell is made by connecting a half-cell of X in $XCl_2(aq)$ to a half-cell of Z in $ZCl_2(aq)$. Deduce the overall equation for the reaction taking place when the cell is operating.

(iii) The standard electrode potential for $Z^{2+}(aq) + 2e^- \rightleftharpoons Z(s)$ is $+0.20\ V$. State which species is oxidized when this half-cell is connected to a standard hydrogen electrode.

(iv) Describe the standard hydrogen electrode including a fully labelled diagram.

c. (i) State the half-equation for the reaction that occurs at each electrode. [4]

Positive electrode (anode):

Negative electrode (cathode):

(ii) Suggest, giving a reason, what would happen if the electrodes were changed to aluminium.

d. (i) Determine the mass of copper produced at one of the electrodes in cell 2 if the tin electrode in cell 1 decreased in mass by 0.034 g. [6]

(ii) Compare the colour and the pH of the solutions in cells 2 and 3 after the current has been flowing for one hour.

(iii) Explain your answer given for part (d) (ii).

Colour:

pH:

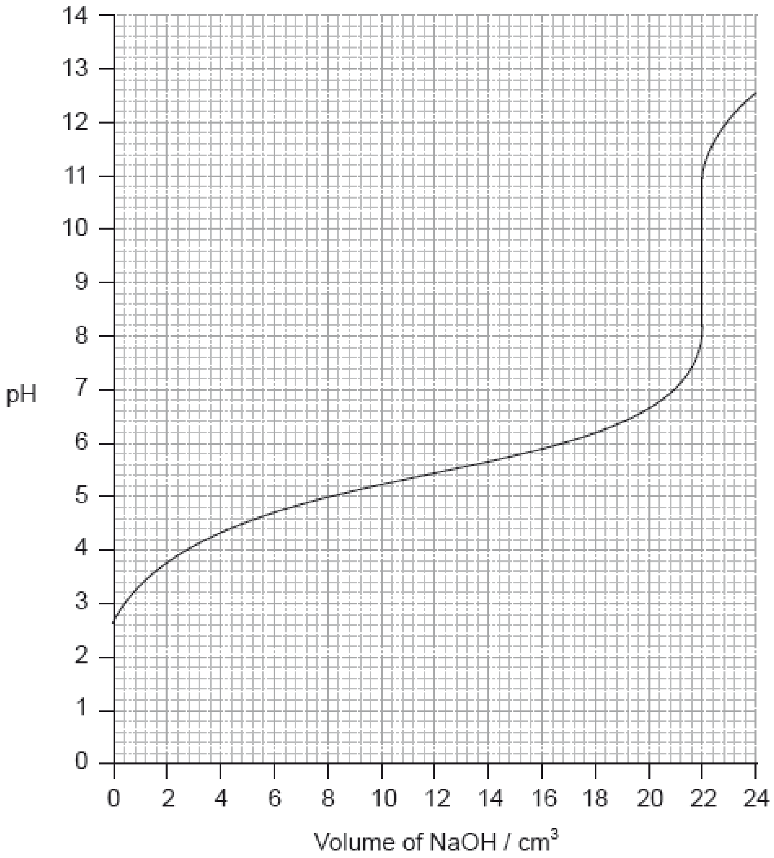
Acids can be described as strong or weak.

a. (i) Outline the difference in dissociation between strong and weak acids of the same concentration. [4]

(ii) Describe **three** tests that can be carried out in the laboratory, and the expected results, to distinguish between $0.10\ \text{mol}\,\text{dm}^{-3}\ \text{HCl(aq)}$ and $0.10\ \text{mol}\,\text{dm}^{-3}\ \text{CH}_3\text{COOH(aq)}$.

b. Calculate the pH, using table 15 of the data booklet, of a solution of ethanoic acid made by dissolving 1.40 g of the acid in distilled water to make a $500\ \text{cm}^3$ solution. [4]

c.i. Determine the pH at the equivalence point of the titration and the $\text{p}K_\text{a}$ of an unknown acid using the acid-base titration curve below. [3]



c.ii. Identify, using table 16 of the data booklet, a suitable indicator to show the end-point of this titration. [1]

c.iii Describe how an indicator, that is a weak acid, works. Use Le Chatelier's principle in your answer. [2]

d.i. State the formula of the conjugate base of chloroethanoic acid, $CH_2ClCOOH$. [1]

d.ii. Identify, with a reason, whether chloroethanoic acid is weaker or stronger than ethanoic acid using table 15 of the data booklet. [1]

d.iii Determine the pH of the solution resulting when $100\ cm^3$ of $0.50\ mol\,dm^{-3}$ $CH_2ClCOOH$ is mixed with $200\ cm^3$ of $0.10\ mol\,dm^{-3}$ NaOH. [4]

e. Describe how chlorine's position in the periodic table is related to its electron arrangement. [2]

f. SCl_2 and $SClF_5$ are two sulfur chloride type compounds with sulfur having different oxidation states. Predict the name of the shape, the bond angle and polarity of these molecules. [[N/A

This question is about the compounds of some period 3 elements.

a. State the equations for the reactions of sodium oxide with water and phosphorus(V) oxide with water. [2]

b.i. Explain why the melting point of phosphorus(V) oxide is lower than that of sodium oxide in terms of their bonding and structure. [2]

b.ii Predict whether phosphorus(V) oxide and sodium oxide conduct electricity in their solid and molten states. Complete the boxes with "yes" or "no". [2]

	Phosphorus(V) oxide	**Sodium oxide**
Solid state	. . . .	. . . .
Molten state	. . . .	. . . .

c. Predict and explain the pH of the following aqueous solutions, using equations to support your answer. [4]

Ammonium chloride, $NH_4Cl(aq)$:

Sodium methanoate, $HCOONa(aq)$:

Consider the following list of organic compounds.

Compound 1: $CH_3CH_2CH(OH)CH_3$

Compound 2: $CH_3CH_2COCH_3$

Compound 3: $CH_3CH_2CH_2OH$

Compound 4: $CH_3CH_2CH_2CHO$

a. Apply IUPAC rules to state the names of the four compounds. [4]

Compound	Name
$CH_3CH_2CH(OH)CH_3$	. . . .
$CH_3CH_2COCH_3$	. . . .
$CH_3CH_2CH_2OH$	. . . .
$CH_3CH_2CH_2CHO$	. . . .

b. (i) Define the term *structural isomers*. [2]

(ii) Identify the two compounds in the list that are structural isomers of each other.

c. (i) Determine the organic product formed when each of the compounds is heated under reflux with excess acidified potassium dichromate(VI). [5]

If no reaction occurs write NO REACTION in the table.

Compound	Organic product
$CH_3CH_2CH(OH)CH_3$	. . . .
$CH_3CH_2COCH_3$	. . . .
$CH_3CH_2CH_2OH$	. . . .
$CH_3CH_2CH_2CHO$	. . . .

(ii) Describe the colour change during the reactions that occur in part (i).

f. (i) Pentanoic acid reacts with ethanol. State the structural formula of the organic product and the name of the functional group it contains. [3]

(ii) State the type of reaction in part (i).

g. Describe what is meant by a weak Brønsted-Lowry base, including an equation for the reaction of ammonia with water. [3]

Bleaches in which chlorine is the active ingredient are the most common, although some environmental groups have concerns about their use.

In aqueous chlorine the equilibrium below produces chloric(I) acid (hypochlorous acid), HOCl, the active bleach.

$$\mathrm{Cl_2(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)}$$

Aqueous sodium chlorate(I), NaOCl, the most common active ingredient in chlorine based bleaches, oxidizes coloured materials to colourless products while being reduced to the chloride ion. It will also oxidize sulfur dioxide to the sulfate ion.

The standard electrode potential for the reduction of the chlorate(V) ion to the chloride ion is $+1.49\ \mathrm{V}$.

a. (i) Describe the colour change that occurs when aqueous chlorine is added to aqueous sodium bromide. [3]

(ii) Outline, with the help of a chemical equation, why this reaction occurs.

b.i. Chloric(I) acid is a weak acid, but hydrochloric acid is a strong acid. Outline how this is indicated in the equation above. [1]

b.ii. State a balanced equation for the reaction of chloric(I) acid with water. [1]

b.iii. Outline, in terms of the equilibrium in aqueous chlorine, why it is dangerous to use an acidic toilet cleaner in combination with this kind of bleach. [2]

b.iv. Suggest why a covalent molecule, such as chloric(I) acid, is readily soluble in water. [2]

b.v. Partial neutralization of chloric(I) acid creates a buffer solution. Given that the $\mathrm{p}K_\mathrm{a}$ of chloric(I) acid is 7.53, determine the pH of a solution that has $[\mathrm{HOCl}] = 0.100\ \mathrm{mol\,dm^{-3}}$ and $[\mathrm{ClO^-}] = 0.0500\ \mathrm{mol\,dm^{-3}}$. [4]

b.vi. Describe, using HIn to represent the indicator in its acid form, why an indicator changes colour when excess alkali is added. [3]

c. (i) Deduce a balanced equation for the reaction between the chlorate(I) ion and sulfur dioxide from the appropriate half-equations. [6]

(ii) State the initial and final oxidation numbers of both chlorine and sulfur in the final equation.

Element	Initial oxidation number	Final oxidation number
Chlorine		
Sulfur		

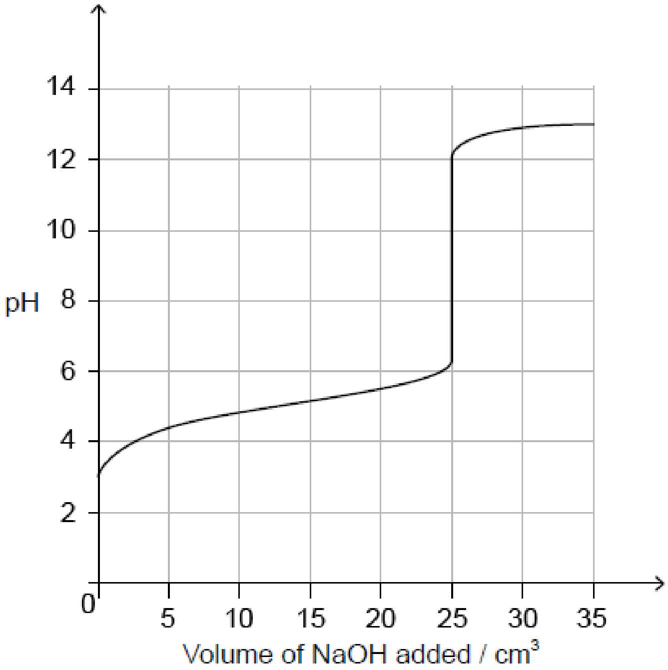
d. (i) Define the term *standard electrode potential*. [3]

(ii) Referring to Table 14 of the Data Booklet, deduce, giving a reason, whether the oxidation of the chromium(III) ion to the dichromate(VI) ion by the chlorate(V) ion is energetically feasible.

Soluble acids and bases ionize in water.

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

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



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

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

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

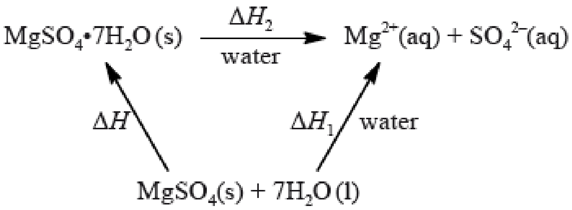
c. The pK_a of an anthocyanin is 4.35. Determine the pH of a 1.60 × 10^{-3} mol dm^{-3} solution to two decimal places. [3]

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

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

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

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



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

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

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

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

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

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

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

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

Lewis (electron dot) structure:

Shape:

Bond angle:

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

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

Nitrogen monoxide reacts at 1280 °C with hydrogen to form nitrogen and water. All reactants and products are in the gaseous phase.

The gas-phase decomposition of dinitrogen monoxide is considered to occur in two steps.

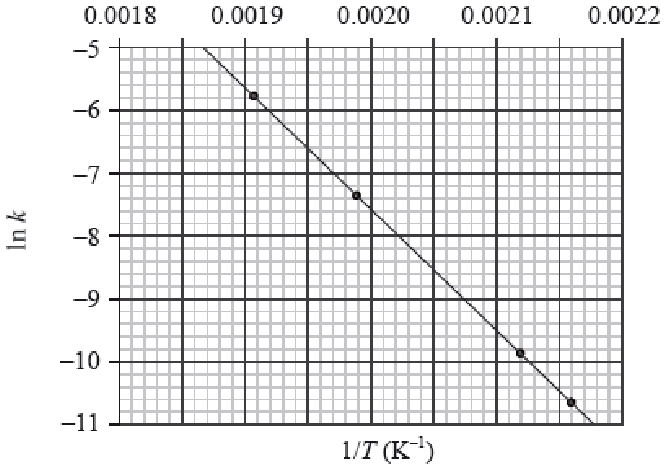
$$\text{Step 1:}\quad N_2O(g) \xrightarrow{k_1} N_2(g) + O(g)$$
$$\text{Step 2:}\quad N_2O(g) + O(g) \xrightarrow{k_2} N_2(g) + O_2(g)$$

The experimental rate expression for this reaction is rate $= k[N_2O]$.

The conversion of CH_3NC into CH_3CN is an exothermic reaction which can be represented as follows.

$$CH_3{-}N{\equiv}C \rightarrow \text{transition state} \rightarrow CH_3{-}C{\equiv}N$$

This reaction was carried out at different temperatures and a value of the rate constant, k, was obtained for each temperature. A graph of $\ln k$ against $1/T$ is shown below.



a.i. Define the term *rate of reaction*. [1]

a.ii. State an equation for the reaction of magnesium carbonate with dilute hydrochloric acid. [1]

a.iii. The rate of this reaction in (a) (ii), can be studied by measuring the volume of gas collected over a period of time. Sketch a graph which shows how the volume of gas collected changes with time. [1]

a.iv. The experiment is repeated using a sample of hydrochloric acid with double the volume, but half the concentration of the original acid. Draw a second line on the graph you sketched in part (a) (iii) to show the results in this experiment. Explain why this line is different from the original line. [4]

b.i. The kinetics of the reaction were studied at this temperature. The table shows the initial rate of reaction for different concentrations of each reactant. [4]

Deduce the order of the reaction with respect to NO and $\mathrm{H_2}$, and explain your reasoning.

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

b.iii. Determine the value of the rate constant for the reaction from Experiment 3 and state its units. [2]

c.i. Identify the rate-determining step. [1]

c.ii. Identify the intermediate involved in the reaction. [1]

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

d.ii. Construct the enthalpy level diagram and label the activation energy, E_a, the enthalpy change, ΔH, and the position of the transition state. [3]

d.iii. Describe qualitatively the relationship between the rate constant, k, and the temperature, T. [1]

d.iv. Calculate the activation energy, E_a, for the reaction, using Table 1 of the Data Booklet. [4]

When nitrogen gas and hydrogen gas are allowed to react in a closed container the following equilibrium is established.

$$\mathrm{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)}\ \Delta H = -92.6\ \mathrm{kJ}$$

a.i. Outline **two** characteristics of a reversible reaction in a state of dynamic equilibrium. [2]

a.ii. Predict, with a reason, how each of the following changes affects the position of equilibrium. [2]

The volume of the container is increased.

Ammonia is removed from the equilibrium mixture.

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

b. Ammonia is manufactured by the Haber process in which iron is used as a catalyst. [2]

Explain the effect of a catalyst on the rate of reaction.

c. Typical conditions used in the Haber process are 500 °C and 200 atm, resulting in approximately 15% yield of ammonia. [3]

(i) Explain why a temperature lower than 500 °C is **not** used.

(ii) Outline why a pressure higher than 200 atm is **not** often used.

d.i. Deduce the equilibrium constant expression, K_c, for the reaction on page 10. [1]

d.ii. When 1.00 mol of nitrogen and 3.00 mol of hydrogen were allowed to reach equilibrium in a $1.00\ \mathrm{dm^3}$ container at a temperature of 500 °C and a pressure of 1000 atm, the equilibrium mixture contained 1.46 mol of ammonia. [2]

Calculate the value of K_c at 500 °C.

e.i. Define the term *base* according to the Lewis theory. [1]

e.ii. Define the term *weak base* according to the Brønsted–Lowry theory. [1]

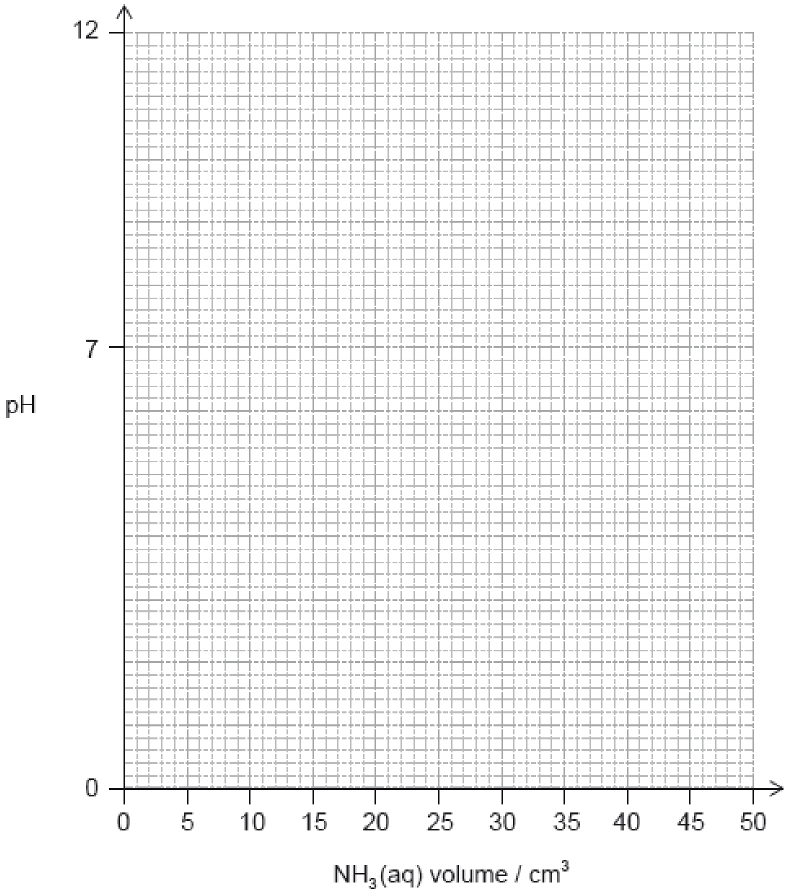
e.iii. Deduce the formulas of conjugate acid-base pairs in the reaction below. [2]

$$\mathrm{CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)}$$

Acid	**Conjugate base**
....	....
....	....

f. Determine the pH of a $0.100\ \mathrm{mol\,dm^{-3}}$ solution of ammonia, $\mathrm{NH_3(aq)}$, using tables 2 and 15 of the data booklet. [4]

g. (i) Sketch the pH titration curve obtained when $50.0\ \mathrm{cm^3}$ of $0.100\ \mathrm{mol\,dm^{-3}\,NH_3(aq)}$ is added to $25.0\ \mathrm{cm^3}$ of $0.100\ \mathrm{mol\,dm^{-3}\,HCl\ (aq)}$. [4]



(ii) Identify an indicator from table 16 of the data booklet that could be used for this titration.

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

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

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

Many organic compounds exist as stereoisomers.

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

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

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

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

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

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

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

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

(ii) Draw the structures of the two stereoisomers of dichloroethene, $\mathrm{C_2H_2Cl_2}$.

(iii) Explain why this type of stereoisomerism exists in $\mathrm{C_2H_2Cl_2}$.

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

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

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

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

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

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

b.i. Deduce the balanced chemical equation for the redox reaction of copper, Cu(s), with nitrate ions, $NO^{3-}(aq)$, **in acid**, to produce copper(II) ions, $Cu^{2+}(aq)$, and nitrogen(IV) oxide, $NO_2(g)$. [2]

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

Oxidizing agent:

Reducing agent:

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

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

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

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

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

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

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

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

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

Positive electrode (anode):

Negative electrode (cathode):

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

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

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

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

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

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

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

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

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

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

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

$$\text{NH}_3\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{NH}_4^{\ +}\,(\text{aq}) + \text{OH}^-\,(\text{aq})$$

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

Weak:

Brønsted–Lowry base:

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

$$\text{P}_4\,(\text{s}) + 3\text{OH}^-\,(\text{aq}) + 3\text{H}_2\text{O}\,(\text{l}) \rightarrow \text{PH}_3\,(\text{g}) + 3\text{H}_2\text{PO}_2^{\ -}\,(\text{aq})$$

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

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

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

P_4:

$H_2PO_2^-$:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

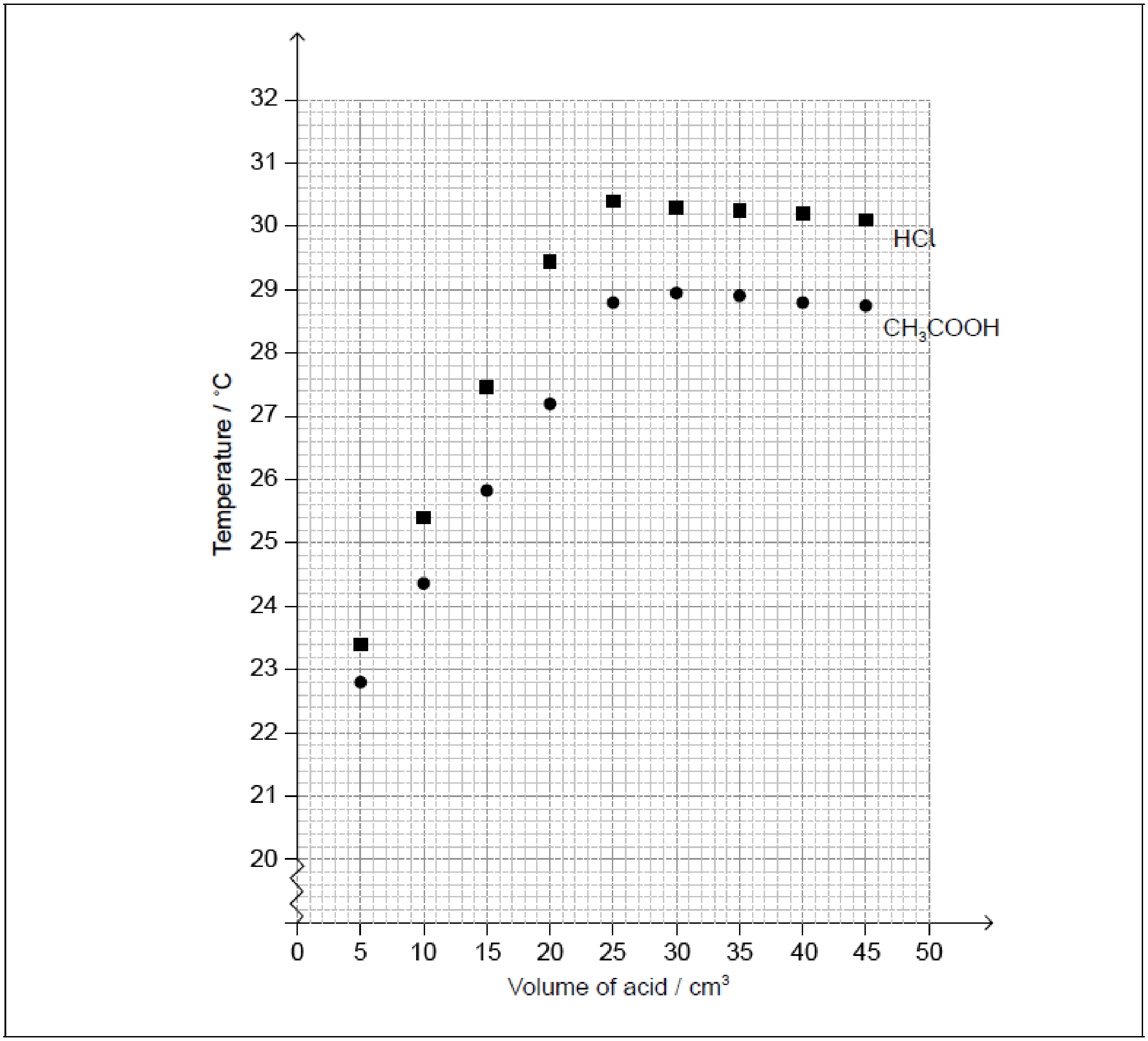
(v) Suggest why oxides of phosphorus are not major contributors to acid deposition.

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

Pre-combustion:

Post-combustion:

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]