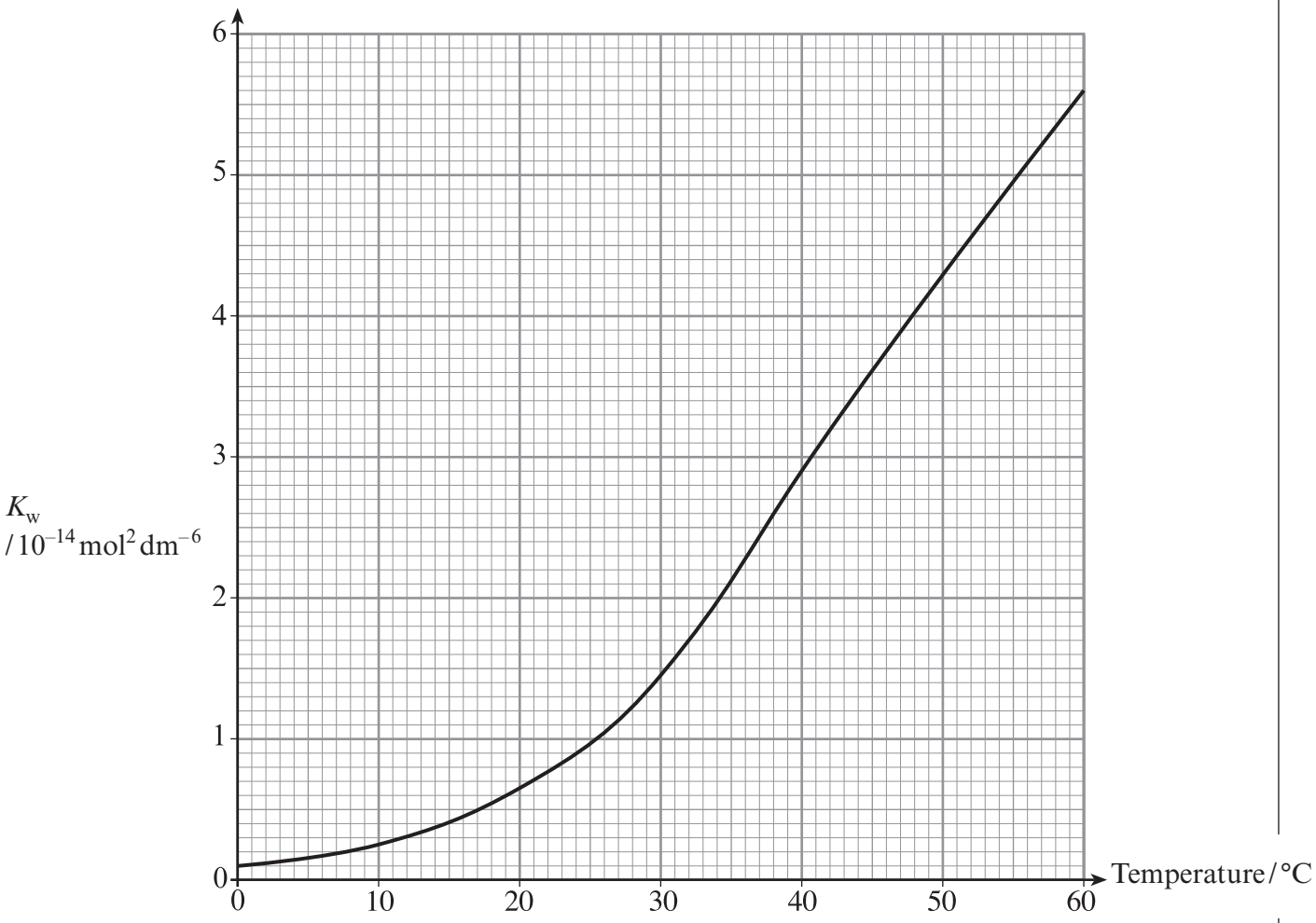
Examiner only

2. *(a)* The diagram shows the variation of the ionic product of water, K_w, with temperature.



(i) Give the expression for the ionic product of water, K_w. [1]

(ii) By reference to the diagram, and giving your reasoning, state whether the ionisation of water is an exothermic or an endothermic process. [1]

.....

.....

(iii) Use the diagram to determine the value (mol^2 dm^{-6}) of K_w at 50 °C. [1]

.....

.....

(iv) Hence calculate [H^+] and the pH of pure water at 50 °C. [2]

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Examiner only

(c) As solids do not affect the position of equilibrium, for the solution equilibrium

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

the simplest expression for the equilibrium constant, K_c, can be written

$$K_c = [Mg^{2+}(aq)][CO_3^{2-}(aq)]$$

(i) Given that the solubility of $MgCO_3$ at 20 °C is 3.16×10^{-3} mol dm^{-3}, state the molar concentrations of magnesium ions, $Mg^{2+}(aq)$, and carbonate ions, $CO_3^{2-}(aq)$, in a saturated $MgCO_3$ solution. [1]

.....

.....

(ii) Hence calculate the value of K_c at 20 °C. [1]

.....

.....

(iii) Giving your reasons, state whether the value of K_c is consistent with the value of the free energy change, ΔG, given for this reaction in *(b)*. [1]

.....

.....

(iv) By applying Le Chatelier's Principle to the chemical equation above, and giving your reasons, state the effect on the solubility of magnesium carbonate of adding sodium carbonate to the solution. [1]

.....

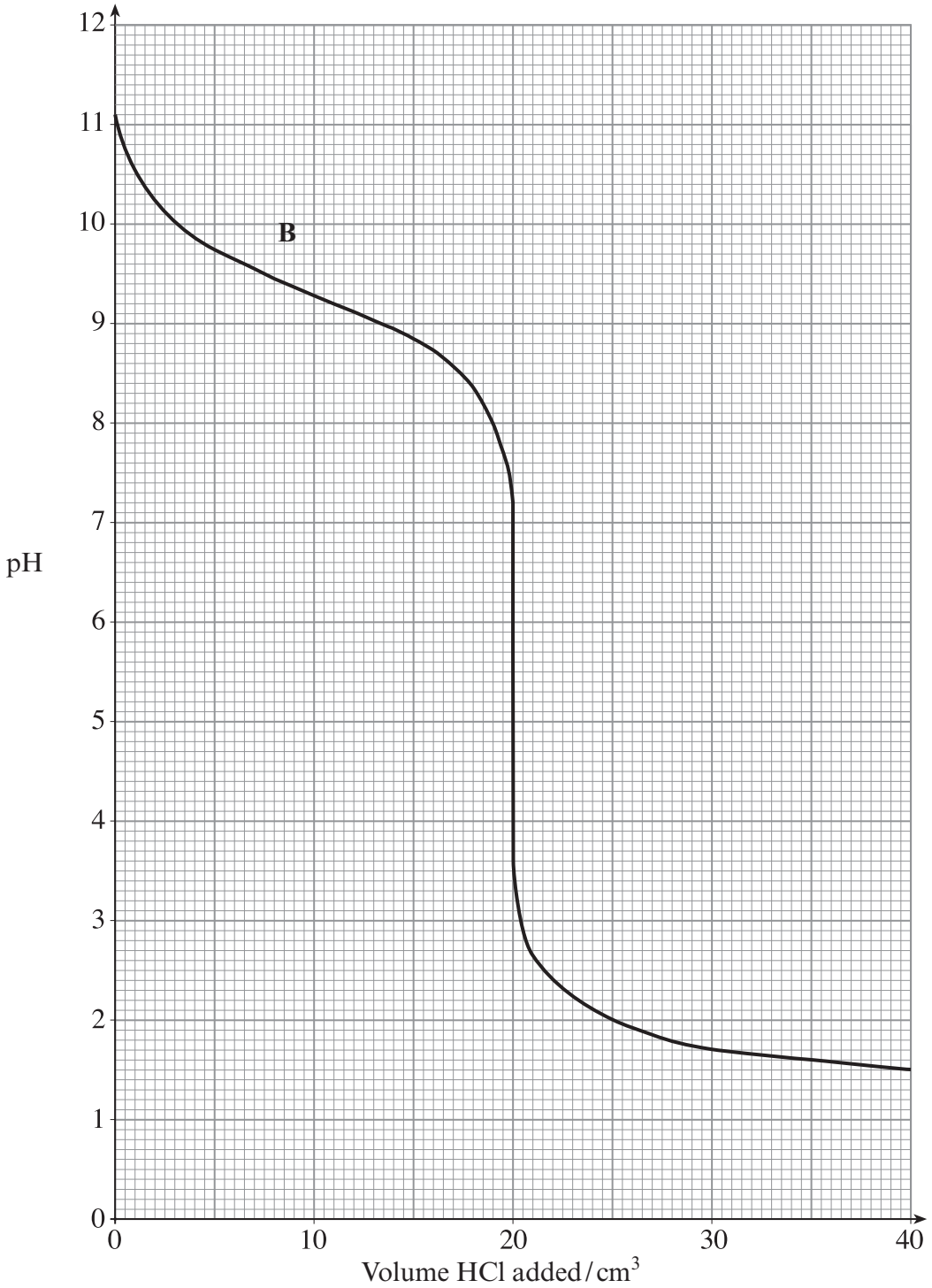
.....

Total [12]

Examiner only

(b) The diagram below shows how pH changes during the course of a titration when hydrochloric acid of concentration 0.100 mol dm^{-3} is added from a burette to 25.0 cm^3 of aqueous ammonia.

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$



(i) Calculate, to **two** significant figures, the concentration of the aqueous ammonia solution. [3]

.....

.....

.....

Examiner only

(ii) Explain why a buffering effect occurs in the region of the curve marked with the letter **B**, where a mixture of $NH_3(aq)$ and $NH_4Cl(aq)$ is present. [3]

.....

.....

.....

.....

.....

(iii) Giving your reasoning, state which of the following indicators would be suitable for the titration of ammonia against hydrochloric acid. [2]

Indicator	pH range
Bromothymol blue	6.0 - 7.6
Methyl red	4.2 - 6.3
Methyl yellow	2.9 - 4.0
Phenolphthalein	8.2 - 10.0

.....

.....

.....

Total [13]

Examiner only

(iii) Two possible mechanisms have been suggested for this reaction. These are shown below.

Mechanism A	*Mechanism B*
$N_2O_5 \rightarrow NO_2 + NO_3^{\bullet}$	$2N_2O_5 \rightarrow 2NO_3^{\bullet} + N_2O_4$
$NO_3^{\bullet} \rightarrow NO^{\bullet} + O_2$	$NO_3^{\bullet} + N_2O_4 \rightarrow NO^{\bullet} + 2NO_2 + O_2$
$NO^{\bullet} + N_2O_5 \rightarrow 3NO_2$	$NO^{\bullet} + NO_3^{\bullet} \rightarrow 2NO_2$

Giving your reasons, state which of the mechanisms is compatible with the rate equation. [2]

.....

.....

.....

(c) The nitrogen dioxide, NO_2, produced in this reaction exists in dynamic equilibrium with dinitrogen tetroxide, N_2O_4. *(line 24)*

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

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

(ii) State and explain the effect of increasing the temperature on the value of K_p. [2]

.....

.....

.....

(iii) At a temperature of 373 K, the partial pressure of a pure sample of NO_2 was 3.00×10^5 Pa. When the mixture was allowed to reach equilibrium, the partial pressure of the remaining NO_2 was 2.81×10^5 Pa.

Calculate the value of K_p, stating its units. [3]

.....

.....

.....

Units .....

Total [15]

5. *(a)* Give a current use for a named compound of chlorine. [1]

(b) Chlorine gas, Cl_2, is used in the industrial preparation of bromine, Br_2. Sea water contains small amounts of bromide ions and by bubbling chlorine gas through the sea water these can be converted to Br_2.

(i) Write an ionic equation for the reaction occurring. [1]

(ii) Use the standard electrode potentials, $E^{\ominus}$, listed below to explain why chlorine can react with bromide ions but iodine cannot react with bromide ions. [3]

Half-equation	$E^{\ominus}$ / V
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36

(c) Sodium chloride and sodium iodide are both compounds which contain halide ions.

(i) Silver nitrate solution may be used to differentiate between solutions of sodium chloride and sodium iodide. Give the observations that would be expected in **both** cases. [1]

(ii) Both sodium chloride and sodium iodide react with concentrated sulfuric acid. The observations made during both reactions are very different. Discuss the reactions occurring. Your answer should include

- the observations made during both reactions,
- the identities of any products,
- the reasons for any differences in the reactions that occur. [5]

(QWC) [1]

(d) Chlorine produces a range of oxoacids, including chloric(I) acid, HOCl, and chloric(VII) acid, $HClO_4$. Chloric(I) acid is considered to be a weak acid whilst chloric(VII) acid is considered to be a strong acid.

(i) What is meant by the term *strong acid*? [1]

(ii) Write an expression for the acid dissociation constant, K_a, of chloric(I) acid, HOCl. [1]

(iii) The pH of a solution of chloric(I) acid of concentration 0.100 mol dm^{-3} was found to be 4.23. Calculate the concentration of hydrogen ions in this solution. [2]

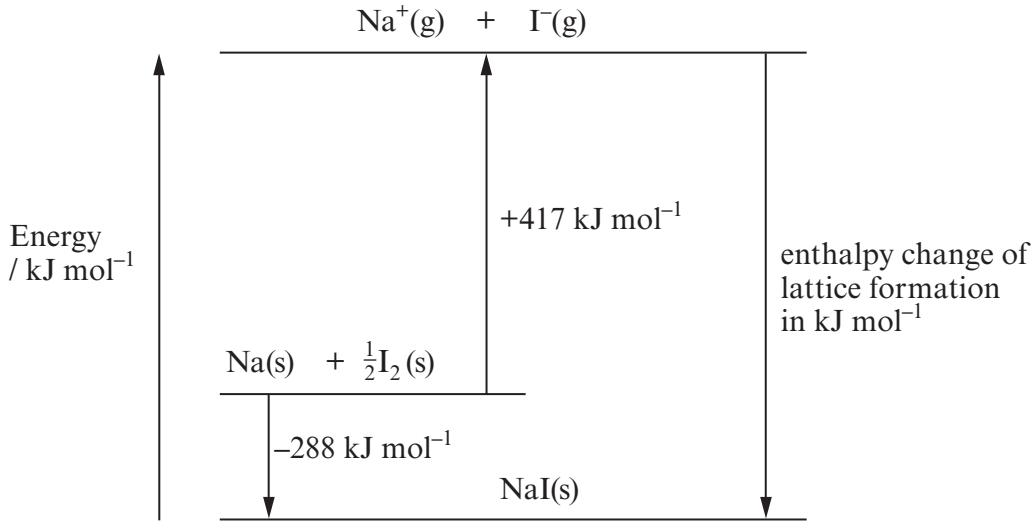
(iv) Using the information from part (iii), calculate the value of the acid dissociation constant, K_a, for chloric(I) acid. [2]

(v) When the weak acid HOCl reacts with the strong base sodium hydroxide it forms the salt sodium chlorate(I), NaOCl. Suggest a pH value for a solution of NaOCl, giving a reason for your answer. [2]

Total [20]

Examiner only

2. *(a)* The diagram shows an outline of the Born-Haber cycle for the formation of sodium iodide (NaI) from its elements.



Use the information given to calculate the enthalpy change of lattice formation (in kJ mol^{-1}) of sodium iodide. [2]

.....

.....

1095 010005

(b) Sodium iodide is very soluble in water at room temperature.

(i) Complete the sentence below using the relevant enthalpy terms.

For a compound to be very soluble in water the value of the enthalpy of

..... will be greater than the enthalpy of .....

[1]

(ii) Aqueous solutions of sodium iodide become yellow in the presence of oxygen due to the slow production of iodine.
One suggested reason for this is that a low concentration of hydrogen ions in the solution produces iodine according to the equation below.

$$4H^+(aq) + 4I^-(aq) + O_2(aq) \rightleftharpoons 2I_2(aq) + 2H_2O(l)$$

Use Le Chatelier's principle to suggest a reagent that you could add, apart from water, to decrease the amount of yellow iodine present. Explain your choice. [2]

.....

.....

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.....

(e) Solutions containing aqueous aluminium ions are weakly acidic because of the dissociation of one of the coordinated water molecules.

$$[Al(H_2O)_6]^{3+}(aq) \quad \rightleftharpoons \quad [Al(H_2O)_5(OH)]^{2+}(aq) \quad + \quad H^+(aq)$$

The acidity of this solution has been used to stop bleeding from minor cuts.

The expression for the equilibrium constant, in terms of concentrations, for the above system is shown below.

$$K_c \quad = \quad \frac{\left[\,[Al(H_2O)_5(OH)\,]^{2+}(aq)\right]\left[H^+(aq)\right]}{\left[\,[Al(H_2O)_6]^{3+}(aq)\right]}$$

Use this expression to calculate the pH of a solution of aluminium ions of concentration 0.10 mol dm^{-3}. The equilibrium constant, K_c, for this system is 1.26×10^{-5} mol dm^{-3}. [3]

Total [20]

5. *(a)* A student obtained some measurements of the partial pressures of reactants and products for the reaction between sulfur(IV) oxide and nitrogen(IV) oxide.

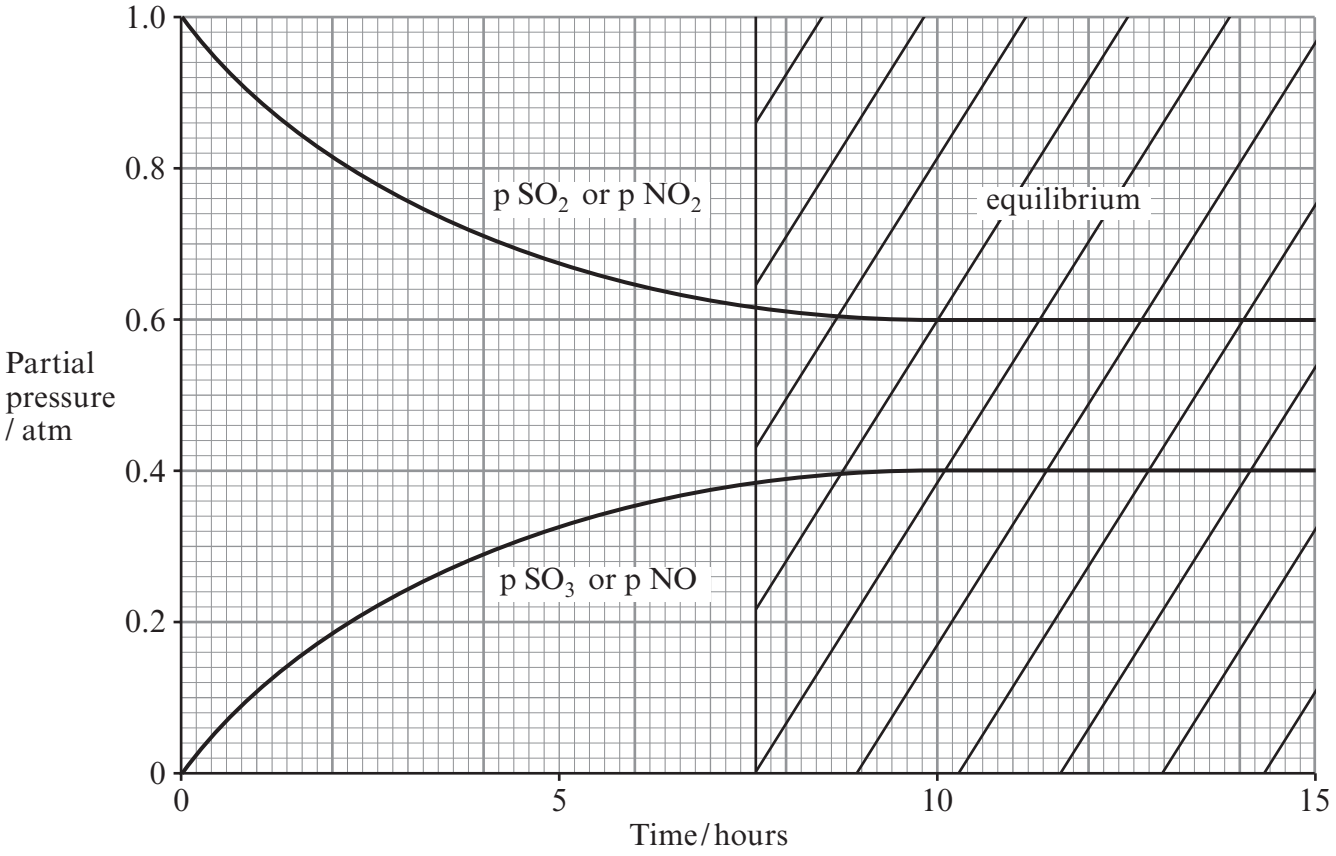
$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

The numerical value of K_p for this reaction is 2.5.

(i) Give the expression for the equilibrium constant in terms of partial pressures, K_p, stating its units (if any). [2]

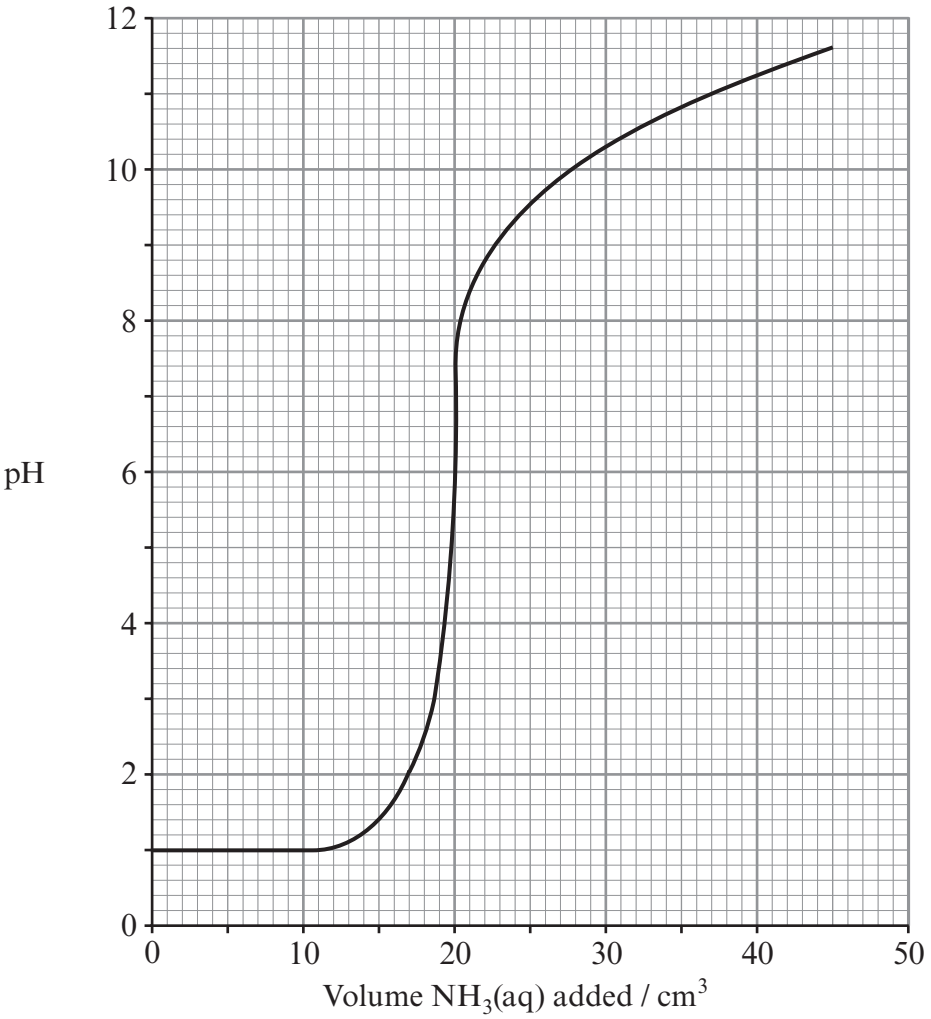
(ii) He decided to present his results in the form of the diagram below.

State the **two** things that are wrong with this diagram, explaining your answer. [4]



(iii) The enthalpy change for this reaction is –41 kJ mol^{-1}. State and explain how the value of the equilibrium constant would change (if at all) when the reaction is run at a higher temperature. [2]

(b) The acid-base titration curve for the reaction between aqueous solutions of nitric acid, HNO_3, and ammonia, both of concentration 0.100 mol dm^{-3}, is shown in the diagram. In this strong acid-weak base system, aqueous ammonia was added to 20.0 cm^3 of aqueous nitric acid.



(i) Describe and explain the shape of the curve obtained when aqueous ammonia is added to the aqueous nitric acid. [3]

QWC [1]

(ii) Deduce, using information obtained from the graph, the mole ratio of the two reactants in this titration. Explain your reasoning. [2]

(iii) I Explain why the pH of a solution of ammonium nitrate is not 7. [1]

II Use the graph to state the pH of the ammonium nitrate solution obtained at the equivalence point. [1]

(iv) Use your answer to (iii) to state the colour obtained if a few drops of the acid-base indicator bromophenol blue are added to the ammonium nitrate solution, giving the reason for your answer. [1]

pH	Colour
$\leqslant$ 2.8	yellow
$\geqslant$ 4.7	blue

(c) Ammonium nitrate (M_r = 80) is used in 'cold packs' to give a cooling effect for sports injuries. The solid crystals are added to water producing an endothermic reaction.

A typical 'cold pack' contains 40 g of ammonium nitrate that is dissolved in water to make 200 g of the solution. Calculate the molar concentration of the ammonium nitrate solution and hence the drop in temperature that occurs when this pack is used.

[1 mole of ammonium nitrate dissolved in water to make 1 kg of solution produces a drop in temperature of 6.2 °C] [3]

Total [20]

Total Section B [40]

Examiner only

SECTION A

Answer **all** *questions in the spaces provided.*

1. Halogens and their compounds take part in a wide variety of reactions.

(a) Give the chemical name of a chlorine-containing compound of commercial or industrial importance. State the use made of this compound. [1]

.....

.....

(b) Hydrogen reacts with iodine in a reversible reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

An equilibrium was established at 300 K, in a vessel of volume 1 dm^3, and it was found that 0.311 mol of hydrogen, 0.311 mol of iodine and 0.011 mol of hydrogen iodide were present.

(i) Write the expression for the equilibrium constant in terms of concentration, K_c. [1]

(ii) Calculate the value of K_c at 300 K. [1]

K_c = ...

(iii) What are the units of K_c, if any? [1]

.....

(iv) Equilibria of H_2, I_2 and HI were set up at 500 K and 1000 K and it was found that the numerical values of K_c were 6.25×10^{-3} and 18.5×10^{-3} respectively.

Use these data to deduce the sign of ΔH for the forward reaction. Explain your reasoning. [3]

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.....

3. *Read the passage below and then answer the questions in the spaces provided.*

Acids Through The Ages

The ancient Greeks started to classify materials as salt-tasting, sweet-tasting, sour-tasting and bitter-tasting. In this classification acids were those considered to be sour-tasting – the name comes from the Latin *acere*.

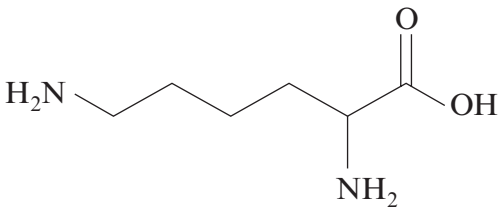
Taste continued to be an important consideration – even today many people would think of the sour taste of a lemon as being typical of an acid. However it was found that, as well as taste, these compounds had other properties in common. The dye litmus had been extracted from lichens and it was found that acids changed the colour of this to red. They also corroded metals.

Many acids were identified – citric acid could be extracted from citrus fruit and methanoic acid could be extracted, by distillation, from red ants. Methanoic acid used to be called formic acid since the biological term for an ant is *formica*.

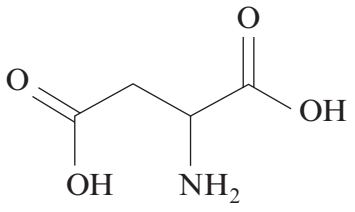
The modern classification of acids is based on the theory suggested by Lowry and Brønsted although more recent classifications, based on electron pair donation, have been suggested by Lewis.

Using the Lowry-Brønsted classification both citric acid and methanoic acid are described as being weak. For methanoic acid, HCOOH, the value of the acid dissociation constant, K_a, is 1.75×10^{-4} mol dm^{-3}.

Acids have a wide variety of uses in modern chemistry. They can, for example, be used as catalysts in hydrolysis reactions and work is currently being done to investigate the possibility of obtaining biofuels by the hydrolysis of farm waste such as straw. In some situations however acids can destroy catalytic effects. The tertiary structure and therefore the shape of the active sites of some enzyme catalysts can be maintained by ionic attractions. This could arise, for example, when the enzyme involves the amino acids lysine and aspartic acid. The NH_2 on the lysine can be protonated to give a positive ion, whilst the COOH can be deprotonated to give a negative ion. Attraction between oppositely charged ions holds the shape but if the pH is altered and one of the charges is lost the shape can change and the enzyme becomes denatured.



lysine



aspartic acid

The possible alteration of the shapes of molecules in biological systems means that it is important that the pH of, for example shampoos, is maintained within a small range. For best results shampoo should stay at a pH just below 7.

- End of passage -

Examiner only

(a) State what is meant by a Lowry-Brønsted acid. *(line 12)* [1]

.....

.....

(b) Define pH. [1]

.....

.....

(c) David and Peter were discussing acids and bases. David said that you could decide whether an acid was strong or weak by measuring the pH of the acid solution. He said that the strong acid would have a lower pH. Peter said that he felt that the strength of the acid was not the only factor that affected pH.

Discuss the factors that affect pH. [4]
QWC [1]

.....

.....

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.....

(d) Methanoic acid is a weak acid.

(i) Write the expression for the acid dissociation constant, K_a, of methanoic acid. [1]

(ii) Using the information in *lines 16* and *17* of the article, calculate the pH of 0.10 mol dm^{-3} methanoic acid. [3]

pH = ...

Examiner only

(e) The article *(line 29)* states that it is important to maintain the pH of shampoo within a small range.

(i) What name is given to a system designed to maintain pH within a small range? [1]

.....

(ii) The pH of a shampoo is maintained within a small range by using a weak acid, RCOOH, and its sodium salt, RCOONa.

Explain how this mixture maintains pH within a small range. [3]

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Total [15]

Total Section A [40]

Examiner only

SECTION A

Answer **all** *questions in the spaces provided.*

1. Ammonium salts are very important chemicals as they are used as a nitrogen source in fertilisers.

(a) When cold aqueous sodium hydroxide is added to an ammonium salt, the following equilibrium exists.

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

Identify the **two** acid-base conjugate pairs in the equilibrium. [2]

.....

.....

(b) Ammonium chloride and sodium nitrite react together in aqueous solution to produce nitrogen gas. This can be represented by the ionic equation:

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$

The rate equation for the reaction is given below.

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

(i) Complete the table of data for the above reaction. All experiments were carried out at the same temperature. [3]

	$[NH_4^+(aq)]$ / mol dm^{-3}	$[NO_2^-(aq)]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.200	0.010	4.00×10^{-7}
2		0.010	2.00×10^{-7}
3	0.200		1.20×10^{-6}
4	0.100	0.020	

(ii) Calculate the value of the rate constant, *k*, giving its units. [2]

Value of k = ...

Units .....

Examiner only

2. *(a)* Write an expression for the ionic product of water, K_w, giving its units, if any. [2]

K_w =

Units .....

(b) (i) The value for K_w at 298 K is 1.0×10^{-14}. Explain why the pH of pure water at this temperature has a value of 7. [2]

.....

.....

.....

(ii) Calculate the pH of the final solution if 10 cm^3 of 0.10 mol dm^{-3} hydrochloric acid is added to 990 cm^3 of pure water. [2]

pH = ...

(c) Calculate the pH of a solution which is 0.010 mol dm^{-3} with respect to ethanoic acid and 0.020 mol dm^{-3} with respect to sodium ethanoate at 298 K. [3]

[K_a for ethanoic acid = 1.78×10^{-5} mol dm^{-3} at 298 K]

pH = ...

Examiner only

(d) If 10 cm^3 of 0.10 mol dm^{-3} hydrochloric acid is added to 990 cm^3 of the solution described in *(c)* the change in pH is only 0.06. Explain why this change in pH is much smaller than that in *(b)*(ii). [3]

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Total [12]

12

(e) A flask containing an initial mixture of 0.100 mol of ethanoic acid and 0.083 mol of methanol was kept at 25 °C until the following equilibrium had been established.

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \qquad \Delta H = -3\,kJ\ mol^{-1}$$

The ethanoic acid present at equilibrium required 32.0 cm^3 of a 1.25 mol dm^{-3} solution of sodium hydroxide for complete reaction.

(i) Write an expression for the equilibrium constant, K_c, giving the units, if any. [2]

(ii) Calculate the number of moles of ethanoic acid present at equilibrium. [1]

(iii) Calculate the value of the equilibrium constant, K_c, for this reaction. [2]

(iv) State, giving a reason, what happens to the value of the equilibrium constant, K_c, if the temperature is increased. [1]

Total [20]

Total Section B [40]

END OF PAPER

