8

2 Chlorine dioxide, ClO_2, is a liquid at room temperature and pressure.
In an aqueous solution it is used as a bleach.

(a) In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions, OH^-.

This reaction is carried out three times using different concentrations of the two reactants. The initial rate of each reaction is determined and the results are shown below.

experiment	$[ClO_2(aq)]$ /mol dm^{-3}	$[OH^-(aq)]$ /mol dm^{-3}	initial rate /mol dm^{-3} s^{-1}
1	0.010	0.030	6.00×10^{-4}
2	0.010	0.075	1.50×10^{-3}
3	0.030	0.030	5.40×10^{-3}

(i) For each reactant, deduce the order of reaction. Show your reasoning.

$OH^-(aq)$ .....

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$ClO_2(aq)$ .....

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..... **[4]**

(ii) Deduce the rate equation for the reaction.

..... [1]

(iii) Calculate the rate constant, k, for this reaction. State the units, if any.
Give your answer to an appropriate number of significant figures.

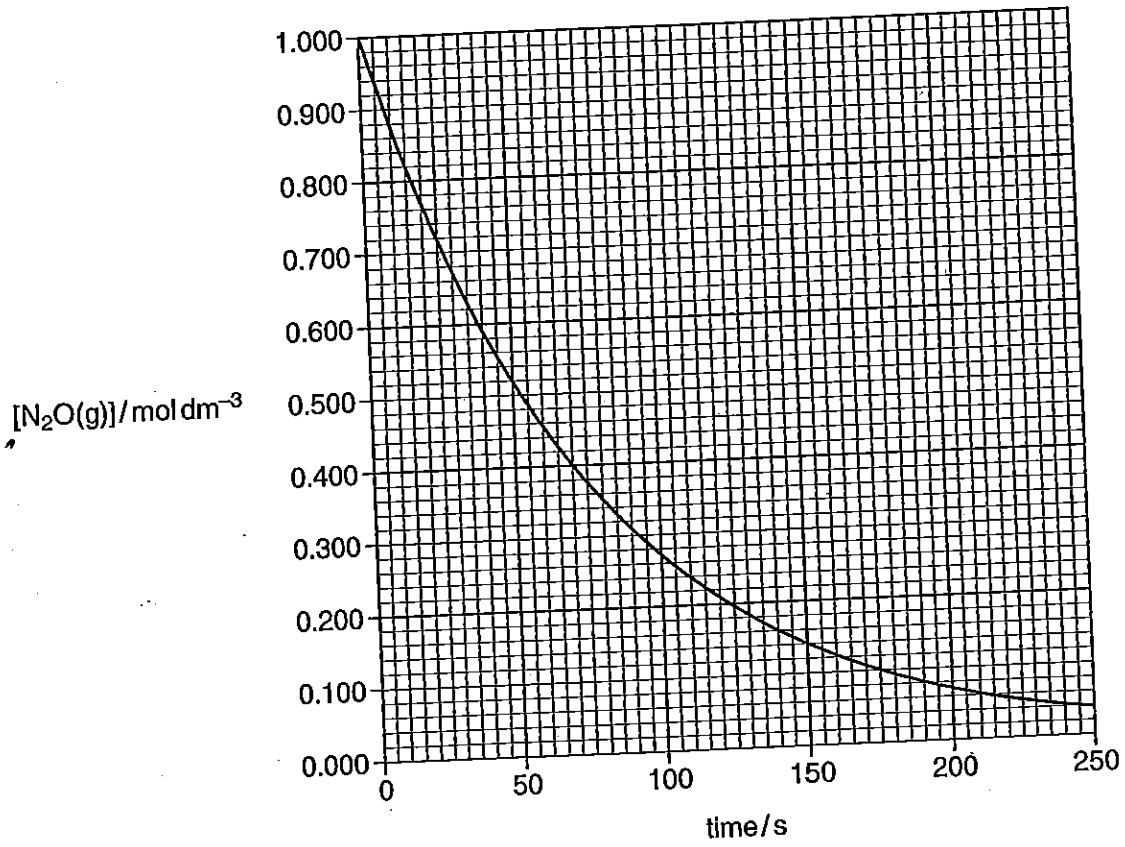
rate constant, k: ..... units: ..... [3]

2 Nitrous oxide, N_2O, is a colourless gas with a mild, pleasant odour and sweet taste. It is widely used as a propellant in aerosol cans of whipped cream.

(a) When heated strongly, nitrous oxide decomposes into its elements.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

This reaction is first order with respect to N_2O. This can be confirmed from the graph below using half-lives.



(i) What is meant by the *half-life* of a reaction?

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..... [1]

(ii) Use this graph to show that this reaction is first order with respect to N_2O.

State the half-life.

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..... [2]

(iii) What would be the effect on the half-life of this reaction of doubling the initial concentration of N_2O?

..... [1]

(b) (i) Write down the rate equation for this reaction.

..... [1]

(ii) Use the graph to work out the rate of reaction, in mol dm^{-3} s^{-1}, at 70 seconds.

Show your working on the graph.

rate = ...mol dm^{-3} s^{-1} [2]

(iii) Calculate the rate constant for this reaction. State the units.

k = ... units: ..... [2]

(c) What evidence is there that the mechanism of this reaction takes place in more than a single step?

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..... [2]

Answer **all** the questions.

1 The decomposition of gaseous hydrogen iodide to form hydrogen and iodine gases is a reversible reaction.

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

(a) Write the expression for K_c for an equilibrium mixture of these three gases.

[1]

(b) A student added 0.50 mol HI(g) to a 1.0 dm^3 container. The container was sealed and the contents were allowed to reach equilibrium at constant temperature.

The student then analysed the equilibrium mixture and found that 0.11 mol $I_2(g)$ was present.

(i) Complete the table below to show the amount of each gas in the equilibrium mixture.

gas	HI(g)	$H_2(g)$	$I_2(g)$
initial amount / mol	0.50	0.00	0.00
equilibrium amount / mol			0.11

[2]

(ii) Calculate K_c to an appropriate number of significant figures. State the units, if any.

K_c = ... units, if any ..... [3]

(c) The student compressed the equilibrium mixture so that its volume was reduced. The temperature was kept constant.

Comment on the value of K_c and the composition of the equilibrium mixture under these new conditions.

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..... [2]

(d) The student repeated the experiment at a higher temperature and found that more $I_2(g)$ was present at equilibrium.

Comment on the value of K_c and explain what additional information this tells you about the reaction.

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..... [2]

5 Ammonia is one of our most important chemicals, produced in enormous quantities because of its role in the production of fertilisers.

Much of this ammonia is manufactured from nitrogen and hydrogen gases using the Haber process. The equilibrium is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

(a) (i) Write an expression for K_c for this equilibrium.

[1]

(ii) Deduce the units of K_c for this equilibrium.

..... [1]

(b) A research chemist was investigating methods to improve the synthesis of ammonia from nitrogen and hydrogen at 500 °C.

- The chemist mixed together nitrogen and hydrogen and pressurised the gases so that their total gas volume was 6.0 dm^3.
- The mixture was allowed to reach equilibrium at constant temperature and without changing the total gas volume.
- The equilibrium mixture contained 7.2 mol N_2 and 12.0 mol H_2.
- At 500 °C, the numerical value of K_c for this equilibrium is 8.00×10^{-2}.

Calculate the amount, in mol, of ammonia present in the equilibrium mixture at 500 °C.

equilibrium amount of NH_3 = ... mol [4]

(c) The research chemist doubled the pressure of the equilibrium mixture whilst keeping all other conditions the same. As expected the equilibrium yield of ammonia increased.

(i) Explain in terms of le Chatelier's principle why the equilibrium yield of ammonia increased.

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..... [2]

(ii) Explain in terms of K_c why the equilibrium yield of ammonia increased.

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..... [3]

16

3 Benzoic acid, C_6H_5COOH, is a weak acid, used for preserving fruit juices.

The acid dissociation constant, K_a, of benzoic acid is 6.30×10^{-5} mol dm^{-3} at 25 °C.

(a) Write the equation for the dissociation of benzoic acid when dissolved in water.

..... [1]

(b) Write the expression for the acid dissociation constant, K_a, of benzoic acid.

[1]

(c) The solubility of benzoic acid in water is 3.40 g dm^{-3} at 25 °C.

Calculate the pH of a saturated solution of benzoic acid in water at 25°C.

[5]

(d) In this question, one mark is available for the quality of use and organisation of scientific terms.

A buffer solution is needed for preserving fruit juice.

A chemist at the fruit juice company prepared a benzoic acid/sodium benzoate buffer with concentrations of 0.105 mol dm^{-3} C_6H_5COOH and 0.125 mol dm^{-3} C_6H_5COONa.

- State what a buffer solution is and explain how this solution acts as a buffer solution. Include equations in your answer.
- Calculate the pH of this benzoic acid/sodium benzoate buffer at 25 °C. Show all your working.

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.... **[8]**

Quality of Written Communication **[1]**

[Total: 16]

Turn over

10

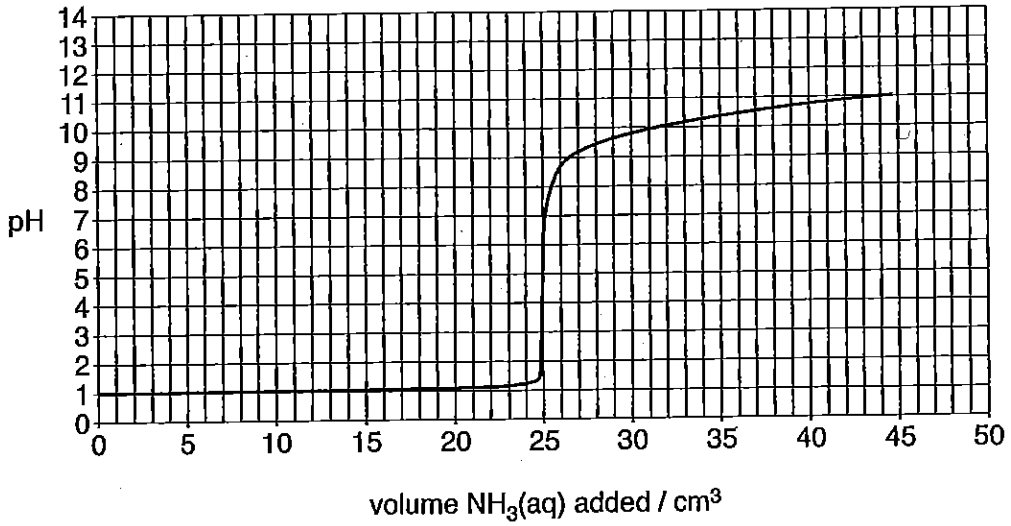
4 Nitric acid, HNO_3, is a strong acid which can also behave as an oxidising agent.

(a) Nitric acid reacts with bases, such as aqueous ammonia, $NH_3(aq)$, to form salts.

A 25.0 cm^3 sample of $HNO_3(aq)$ was placed in a conical flask.

$NH_3(aq)$ was added from a burette until the pH showed little further change.
The NH_3 concentration was the same as the HNO_3 concentration.

The pH curve for this titration is shown below.



(i) Deduce the concentration of the nitric acid.

[1]

(ii) How can you tell from this pH curve that aqueous ammonia is a weak base?

.....

..... [1]

(iii) What is the formula for the salt formed in this reaction?

..... [1]

(iv) The pH ranges for four indicators are shown below.

indicator	pH range
malachite green	0.2–1.8
resazurin	3.8–6.4
metacresol purple	7.4–9.0
alizarin yellow R	10.1–12.0

Which of these four indicators is most suitable for this titration?

..... [1]

(v) The titration was repeated but using $NH_3(aq)$ with **twice** the concentration of the original ammonia solution.

What **two** differences would there be between this titration curve and the one shown in part **(a)**?

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..... [2]

(b) When nitric acid reacts with magnesium metal, different gases are formed, depending on the concentration of the nitric acid. Each reaction producing a gas is a redox reaction.

- With very dilute nitric acid, H_2 gas is evolved.
- With concentrated nitric acid, NO_2 gas is evolved.

(i) Write a full equation and an ionic equation for the reaction of magnesium with very dilute nitric acid.

full equation .....

ionic equation ..... [2]

(ii) Use oxidation numbers to show the reduction that takes place when magnesium reacts with dilute and with concentrated nitric acid.

dilute HNO_3 .....

concentrated HNO_3 ..... [2]

[Total: 10]

(c) In this question, one mark is available for the quality of use and organisation of scientif terms.

A glycolic acid skin-care product has a buffered pH of 4.4.
The buffer contains a solution of glycolic acid and its sodium salt, sodium glycolate.

- Explain what a buffer is and how **this** buffer system works. Include equations in you answer.
- Calculate the proportions of glycolic acid and sodium glycolate in this skin-care product

Glycolic acid has a K_a value of 1.48×10^{-4} mol dm^{-3}.

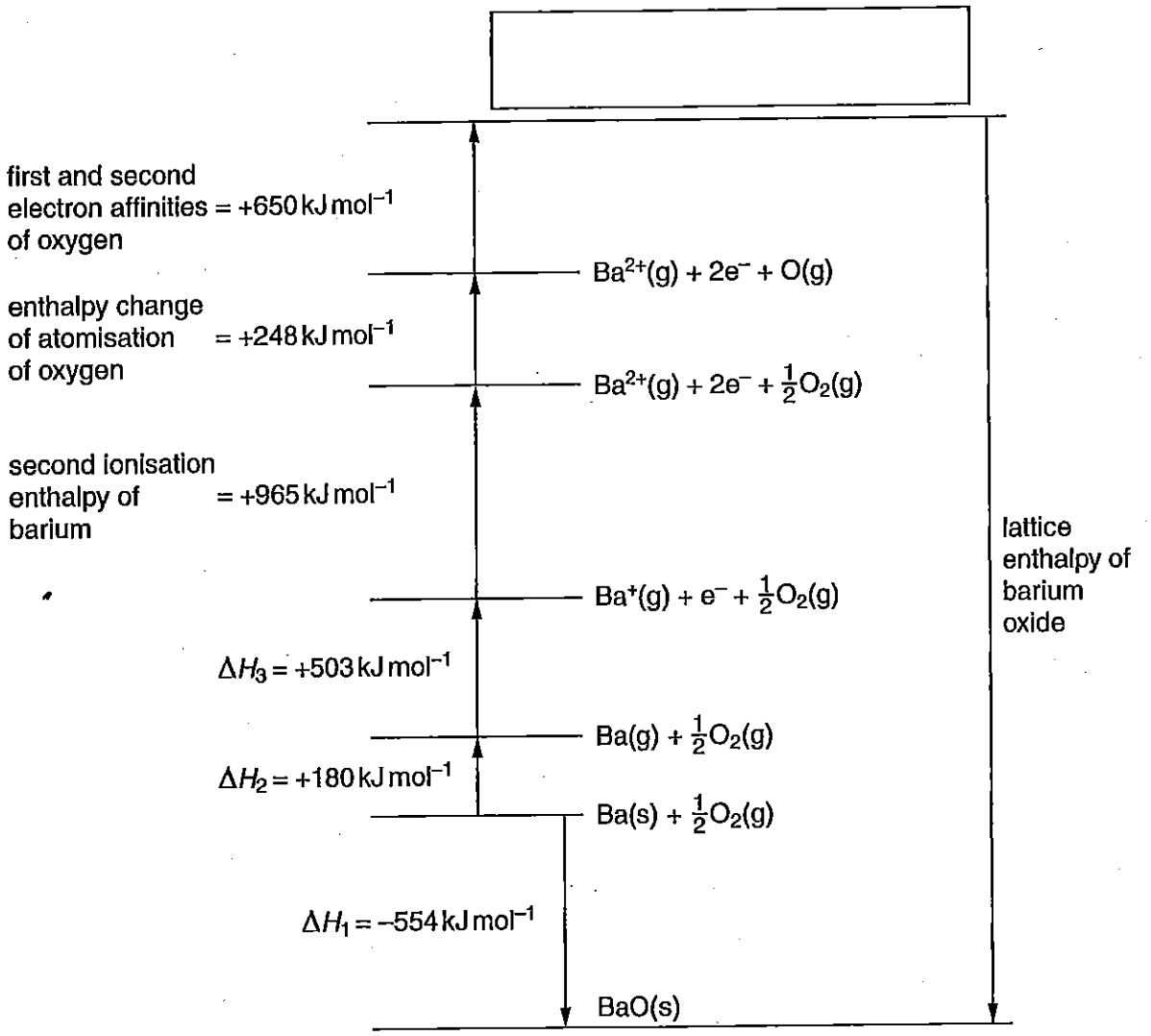
..... [9]

Quality of Written Communication [1]

TURN OVER FOR QUESTION 4(d)

Answer all the questions.

1 The Born-Haber cycle below can be used to calculate the lattice enthalpy for barium oxide.



(a) (i) Write down the name for each of the following enthalpy changes in the Born-Haber cycle above.

ΔH_1 .....

ΔH_2 .....

ΔH_3 ..... [3]

(ii) Write down the missing formulae in the box at the top of the Born-Haber cycle.

Include state symbols. [1]

(b) (i) Use the Born-Haber cycle to calculate the lattice enthalpy of barium oxide.

answer = ... $kJ\,mol^{-1}$ **[2]**

(ii) The lattice enthalpy of barium oxide is different from that of magnesium oxide.

Explain why these lattice enthalpies differ.

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..... **[3]**

(c) Give **one** reason why magnesium oxide is a good material to use for the lining of a furnace.

..... **[1]**

(e) In the industrial production of ammonia, a temperature in the range 400–500 °C is used.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

Standard entropies of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are given in the table below.

substance	$N_2(g)$	$H_2(g)$	$NH_3(g)$
$S/J\,K^{-1}\,mol^{-1}$	191	131	192

(i) Show that the formation of ammonia from nitrogen and hydrogen gases should be feasible at room temperature (25 °C).

[6]

(ii) Explain, in terms of entropy, why this reaction is **not** feasible at very high temperatures.

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..... **[2]**

(iii) Suggest why a temperature of 400–500 °C is used for ammonia production, despite the reaction being feasible at room temperature.

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..... **[1]**

[Total: 22]