

Write your name here

Surname

Other names

Pearson Edexcel
International
Advanced Level

Centre Number

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Candidate Number

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Chemistry

International Advanced Level

Unit 4: Rates, Equilibria and Further Organic Chemistry

Sample Assessment Materials for first teaching September 2018

Time: 1 hour 45 minutes

Paper Reference

WCH14/01

You must have:

Data Booklet, scientific calculator, ruler

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
– *there may be more space than you need.*
- **Show all your working in calculations and include units where appropriate.**

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
– *use this as a guide as to how much time to spend on each question.*
- In questions marked with an **asterisk** (*), marks will be awarded for your ability to structure your answer logically showing how the points that you make are related or follow on from each other where appropriate.
- There is a Periodic Table on the back page of this paper.

Advice

- Read each question carefully before you start to answer it.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ►

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Pearson

SECTION A

Answer **ALL** the questions in this section.

You should aim to spend no more than 20 minutes on this section.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Which compound has the highest boiling temperature?

- ☐ A butanal
- ☐ B butan-1-ol
- ☐ C butanone
- ☐ D butanoic acid

(Total for Question 1 = 1 mark)

2 Which reaction does **not** produce a carboxylic acid?

- ☐ A hydrolysis of an acyl chloride with cold water
- ☐ B hydrolysis of an ester by refluxing with dilute hydrochloric acid
- ☐ C hydrolysis of a nitrile by refluxing with aqueous potassium hydroxide
- ☐ D oxidation of a primary alcohol by refluxing with excess acidified potassium dichromate

(Total for Question 2 = 1 mark)

3 The organic product of the reaction of ethanoyl chloride with ammonia gas is:

- ☐ A ammonium ethanoate
- ☐ B ethanamide
- ☐ C ethanenitrile
- ☐ D methanenitrile

(Total for Question 3 = 1 mark)

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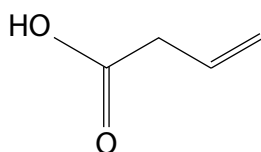
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4 Which compound gives a pale yellow precipitate on warming with a solution of iodine and sodium hydroxide?

- ☐ A CH_3OH
- ☐ B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
- ☐ C $\text{CH}_3\text{CH}_2\text{COCH}_3$
- ☐ D $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

(Total for Question 4 = 1 mark)

5 Lithium tetrahydridoaluminate(III), LiAlH_4 , is used to reduce the compound shown.



The product formed is:

- ☐ A a saturated alcohol
- ☐ B a saturated carboxylic acid
- ☐ C an unsaturated alcohol
- ☐ D an unsaturated ketone

(Total for Question 5 = 1 mark)

6 Carboxylic acids and acyl chlorides both react with alcohols to produce esters. Acyl chlorides are often preferred to carboxylic acids for this reaction because the yield of the ester is usually higher. Which of the following statements is the best explanation for the higher yield?

- ☐ A acyl chlorides react to remove any water produced
- ☐ B the reaction is not reversible
- ☐ C the reaction is less exothermic
- ☐ D the reaction has a higher atom economy

(Total for Question 6 = 1 mark)

7 Polyesters can be made by the reaction of:

- ☐ A diprotic carboxylic acids with a primary alcohol
- ☐ B diprotic carboxylic acids with diols
- ☐ C monoprotic carboxylic acids with triols
- ☐ D monoprotic carboxylic acids with a secondary alcohol

(Total for Question 7 = 1 mark)

8 When mixed in equimolar quantities, which pair of molecules will **not** rotate the plane of plane-polarised light?

- ☐ A
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{array}$

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{array}$
- ☐ B
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{array}$

$\begin{array}{c} \text{Br} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{CH}_3 \\ | \\ \text{C}_2\text{H}_5 \end{array}$
- ☐ C
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ / \quad \backslash \\ \text{H} \quad \text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{array}$

$\begin{array}{c} \text{H} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{Br} \quad \text{CH}_3 \\ | \\ \text{C}_2\text{H}_5 \end{array}$
- ☐ D
- $\begin{array}{c} \text{H} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{array}$

$\begin{array}{c} \text{H} \\ | \\ \text{C} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{Br} \\ | \\ \text{C}_2\text{H}_5 \end{array}$

(Total for Question 8 = 1 mark)

9 In gas chromatography (GC), which one of the following would **increase** the retention time for an alcohol?

- ☐ A increasing the flow rate of the mobile phase
- ☐ B increasing the polarity of the stationary phase
- ☐ C decreasing the polarity of the stationary phase
- ☐ D increasing the polarity of the mobile phase

(Total for Question 9 = 1 mark)

10 Iodine was dissolved in an organic solvent, trichloromethane, and the resulting solution added to an equal volume of deionised water. The mixture was then shaken, producing two immiscible solutions: iodine in water and iodine in trichloromethane.

At equilibrium, the equation for the reaction can be written as:



(a) What is the expression for this equilibrium constant, K_c ?

(1)

- ☐ A $K_c = \frac{[\text{I}_2(\text{trichloromethane})]}{[\text{I}_2(\text{aq})]}$
- ☐ B $K_c = \frac{(\text{I}_2(\text{aq}))}{(\text{I}_2(\text{trichloromethane}))}$
- ☐ C $K_c = \frac{\text{I}_2(\text{aq})}{\text{I}_2(\text{trichloromethane})}$
- ☐ D $K_c = \frac{[\text{I}_2(\text{aq})]}{[\text{I}_2(\text{trichloromethane})]}$

(b) Which statement describes what is happening at equilibrium?

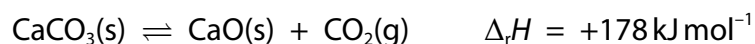
(1)

- ☐ A iodine molecules move from the water to the trichloromethane layer only
- ☐ B iodine molecules move from the trichloromethane to the water layer only
- ☐ C iodine molecules move from the water to the trichloromethane and from the trichloromethane to the water layer.
- ☐ D there is no movement of individual iodine molecules

(Total for Question 10 = 2 marks)

11 Calcium oxide is manufactured by heating limestone at 1000 °C for 30 minutes.

The equation for the reaction is:



(a) The numerical value of the equilibrium constant for this reaction is increased by:

(1)

- ☐ A allowing the carbon dioxide to escape
- ☐ B increasing the heating time
- ☐ C increasing the temperature
- ☐ D reducing the pressure

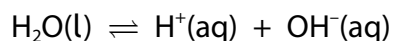
(b) Which is the correct expression for the equilibrium constant, K_c , for this reaction?

(1)

- ☐ A $K_c = [\text{CO}_2]$
- ☐ B $K_c = \frac{1}{[\text{CO}_2]}$
- ☐ C $K_c = \frac{[\text{CaCO}_3]}{[\text{CaO}][\text{CO}_2]}$
- ☐ D $K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$

(Total for Question 11 = 2 marks)

12 The equation for the dissociation of water is:



The ionic product of water, K_w , varies with temperature.

Temperature/°C	$K_w / \text{mol}^2\text{dm}^{-6}$
25	1.01×10^{-14}
30	1.47×10^{-14}
50	5.48×10^{-14}
100	7.16×10^{-14}

What is the pH of pure water at 60°C?

- ☐ A approximately 6.5
- ☐ B exactly 7
- ☐ C approximately 7.4
- ☐ D greater than 7.4

(Total for Question 12 = 1 mark)

13 Iodine reacts with propanone under acid conditions. The reaction is first order with respect to propanone, first order with respect to hydrogen ions and zero order with respect to iodine.

What are the units of the rate constant?

- ☐ A $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
- ☐ B $\text{mol dm}^{-3} \text{s}^{-1}$
- ☐ C s^{-1}
- ☐ D $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

(Total for Question 13 = 1 mark)

14 The halogenoalkane, 2-bromobutane, can be hydrolysed using aqueous sodium hydroxide.

Which technique can be used to follow the progress of this reaction?

- ☐ **A** colorimetry
- ☐ **B** measurement of gas volume change
- ☐ **C** measurement of mass change
- ☐ **D** titration of quenched samples

(Total for Question 14 = 1 mark)

15 What can be deduced from the position of the activation energy on a Maxwell-Boltzmann distribution curve?

- ☐ **A** number of particles in the rate determining step
- ☐ **B** number of successful collisions per second
- ☐ **C** order of reaction
- ☐ **D** proportion of particles with sufficient energy to react

(Total for Question 15 = 1 mark)

16 Which indicator should be used to determine the end point in a titration of a strong acid with a weak base?

- ☐ **A** universal indicator
- ☐ **B** methyl orange
- ☐ **C** phenolphthalein
- ☐ **D** litmus

(Total for Question 16 = 1 mark)

17 Which substance has the highest standard molar entropy?

- ☐ **A** ethane(g)
- ☐ **B** water(s)
- ☐ **C** water(l)
- ☐ **D** water(g)

(Total for Question 17 = 1 mark)

- 18 The element sulfur can exist in two solid, interchangeable, structural forms known as rhombic sulfur and monoclinic sulfur.



The value of ΔS_{total} is for the forward reaction. What can be concluded from this information?

- ☐ A monoclinic sulfur will change quickly into rhombic sulfur
- ☐ B rhombic sulfur could change into monoclinic sulfur but nothing can be deduced about the rate
- ☐ C there can be no change of structural form as they are both solids
- ☐ D monoclinic sulfur could change into rhombic sulfur but nothing can be deduced about the rate

(Total for Question 18 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

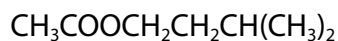
SECTION B

Answer ALL the questions.

Write your answers in the spaces provided.

- 19 One of the compounds responsible for the characteristic smell of bananas is 3-methylbutyl ethanoate.

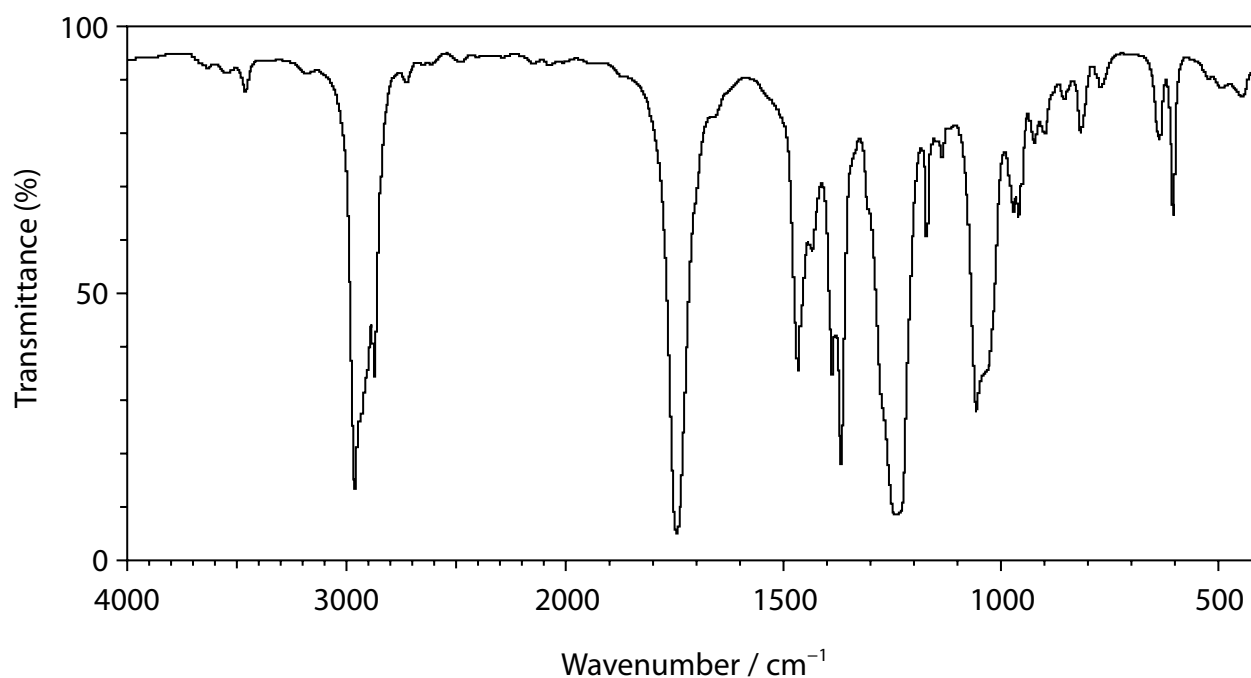
The structural formula of this compound is:



- (a) Draw the **skeletal** formula for 3-methylbutyl ethanoate.

(1)

- (b) The infrared spectrum of a sample of 3-methylbutyl ethanoate is shown below.



- (i) Use this spectrum to identify one peak resulting from a bond in the ester group of 3-methylbutyl ethanoate. Include the relevant bond and its wavenumber range.

(1)

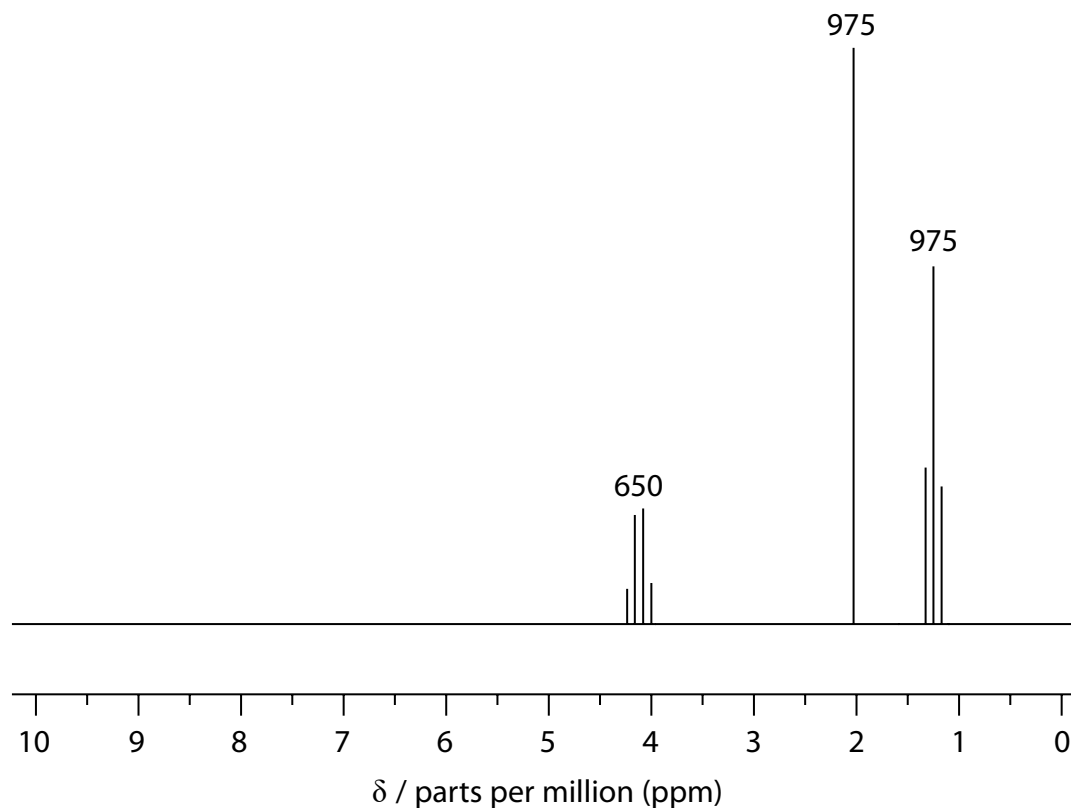
- (ii) 3-methylbutyl ethanoate was synthesised by reacting a suitable carboxylic acid with an alcohol.

Show that its infrared spectrum confirms there is no alcohol remaining in the sample.

(1)

*(c) The high resolution proton nuclear magnetic resonance (NMR) spectrum of a different ester, ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$, is shown.

The numbers over each peak represent their approximate relative areas.



Show that the structure of ethyl ethanoate is consistent with this NMR spectrum, using all the data in the spectrum.

(6)

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(d) Ethyl ethanoate has three isomers which are also esters.

(i) Draw the structures of these three isomers.

(2)

(ii) Explain to what extent it is possible to distinguish between the three isomers using carbon-13 NMR spectroscopy.

(2)

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(Total for Question 19 = 13 marks)

20 This question is about acids.

(a) Calculate the pH of the following acidic solutions. Give your answers to **two** decimal places.

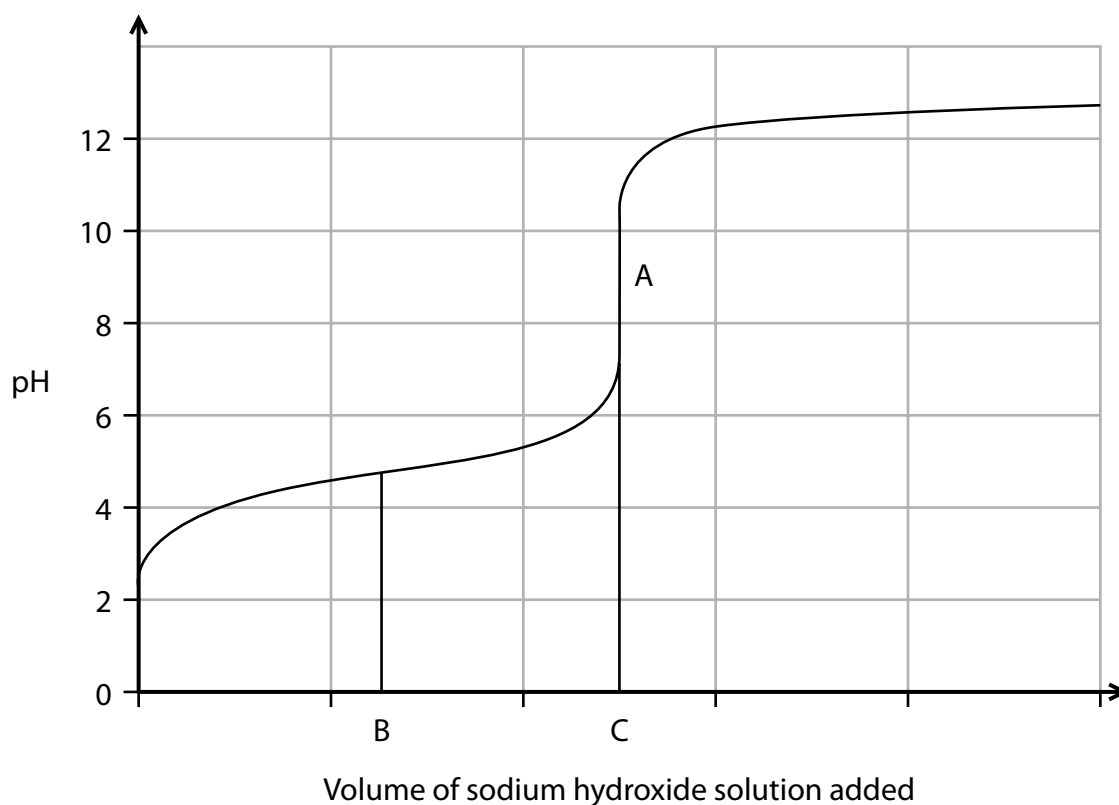
(i) 0.14 mol dm^{-3} solution of hydrochloric acid

(1)

(ii) 0.14 mol dm^{-3} solution of ethanoic acid ($K_a = 1.76 \times 10^{-5} \text{ mol dm}^{-3}$)

(3)

(b) The graph shows the titration curve for a weak acid with a strong base. The equivalence point is A and the volume of alkali added at the equivalence point is C. Volume B is half of volume C.



- (i) Use the graph to determine the dissociation constant, K_a , of the weak acid.

(3)

- (ii) Explain the rapid rise in pH from 2.8 to 4 at the start of the titration.

(2)

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- (c) In another experiment, 10 cm^3 of 1.0 mol dm^{-3} sodium hydroxide was added to 30 cm^3 1.0 mol dm^{-3} propanoic acid ($K_a = 1.3 \times 10^{-5}\text{ mol dm}^{-3}$).

- (i) Calculate the pH of the resulting solution.

(3)

(ii) State one assumption you have made in this calculation.

(1)

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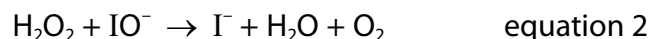
(Total for Question 20 = 13 marks)

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- 21 The mechanism for the rapid decomposition of hydrogen peroxide, H_2O_2 , in the presence of iodide ions, is:



- (a) Write the overall equation for the reaction and hence state the role of the iodide ions.

(2)

- (b) In further experiments, a student calculated the rate constant for the decomposition of hydrogen peroxide at two different temperatures.

Temperature/ $^{\circ}\text{C}$	Rate constant (k) / $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
22.0	4.90×10^{-4}
47.0	2.92×10^{-3}

The rate constant (k) is related to the temperature, T , (in Kelvin) by the following equation:

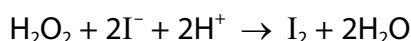
$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \quad R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

Use the data in the table to calculate the activation energy, E_a , for the reaction by a non-graphical method.

Give your answer in kJ mol^{-1} and to an appropriate number of significant figures. Include a sign in your answer.

(4)

- (c) If acid conditions are used, the decomposition of hydrogen peroxide proceeds by a different mechanism. The equation for this reaction is:



This reaction is first order with respect to both iodide ions and hydrogen peroxide.

The progress of this reaction is usually followed by adding a fixed quantity of sodium thiosulfate solution and a little starch solution to the reaction mixture, then timing the appearance of a blue-black colour. This is known as a clock reaction.

- (i) Explain the formation of the blue-black colour and why its appearance is delayed.

(3)

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- (ii) Although the oxidation of thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$) by hydrogen peroxide is thermodynamically favourable, it does not take place in this clock reaction. Suggest a reason for this.

(1)

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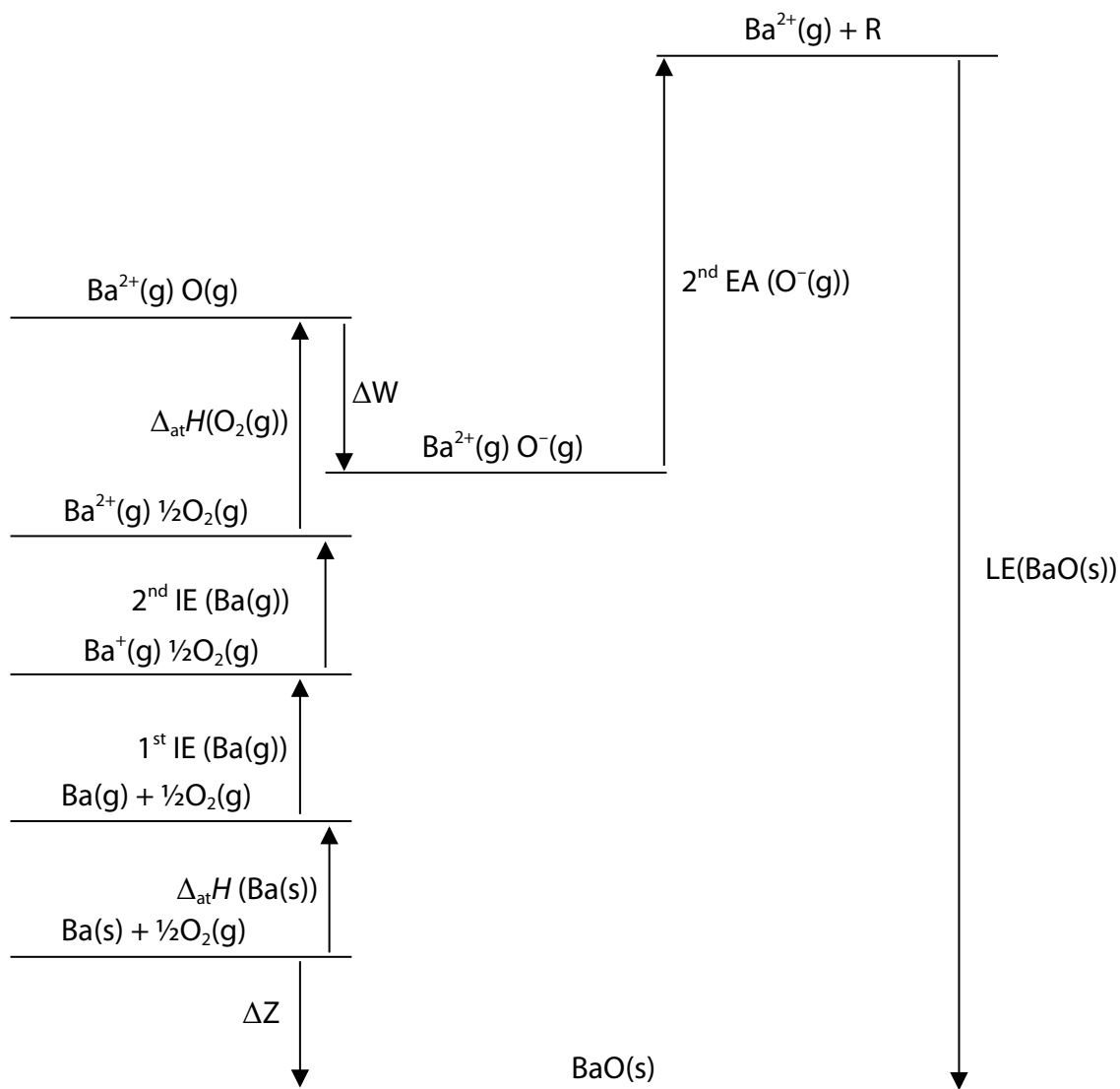
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(Total for Question 21 = 10 marks)

22 Barium oxide is an ionic compound that reacts with water to form barium hydroxide.

(a) A Born-Haber cycle for barium oxide, BaO, is shown.

Some of the detail is missing. The letters **R**, **W** and **Z** represent some missing information.



(i) Identify the missing detail represented by the following letters.

(2)

R

W

- (ii) Use the following data to calculate a value for the quantity ΔZ shown on the Born-Haber cycle.
Include a sign and units in your answer.

(3)

Energy quantity	Enthalpy change / kJ mol^{-1}
Enthalpy change of atomisation of barium, $\Delta_{\text{at}}H(\text{Ba(s)})$	+180.0
Enthalpy change of atomisation of oxygen, $\Delta_{\text{at}}H(\frac{1}{2}\text{O}_2(\text{g}))$	+249.2
First ionisation energy of barium, 1st IE (Ba(g))	+503.0
Second ionisation energy of barium, 2nd IE (Ba(g))	+965.0
ΔW	-141.1
Second electron affinity of oxygen, 2nd EA ($\text{O}^-(\text{g})$)	+798.0
Lattice energy barium oxide, $\Delta_{\text{LE}}H(\text{BaO(s)})$	-3054.0

- (iii) The table gives some information about the lattice energies of barium oxide and magnesium iodide and shows the % difference between the theoretical and experimental values.

	Lattice energy / kJ mol^{-1}		
	Experimental	Theoretical	% difference
BaO(s)	-3054	-3029	0.8
MgI ₂ (s)	-2327	-1944	16.5

Explain why there is closer agreement for barium oxide than for magnesium iodide.

(3)

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(b) The table gives some information about Group 2 ions, M^{2+} , and their hydroxides.

Formula of hydroxide	Lattice energy / kJ mol^{-1}	$\Delta_{\text{sol}}H / \text{kJ mol}^{-1}$	Solubility / mol per 100 g	Ion	$\Delta_{\text{hyd}}H / \text{kJ mol}^{-1}$
Mg(OH)_2	-3000	+150	2.0×10^{-5}	Mg^{2+}	-1930
Ca(OH)_2	-2640	+140	1.6×10^{-4}	Ca^{2+}	-1580
Sr(OH)_2	-2475	+105	3.3×10^{-4}	Sr^{2+}	-1450
Ba(OH)_2	-2230		2.4×10^{-4}	Ba^{2+}	-1360

- (i) Calculate the enthalpy change of solution, $\Delta_{\text{sol}}H$, of Ba(OH)_2 using a fully-labelled Hess's cycle.
 [The hydration enthalpy of the hydroxide ion, $\text{OH}^- = -460 \text{ kJ mol}^{-1}$.]

(4)

- (ii) Explain why strontium hydroxide is slightly soluble in water, even though the enthalpy change of solution is endothermic.

(2)

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(Total for Question 22 = 14 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

Answer ALL the questions.

Write your answers in the spaces provided.

23 This question is about the thermodynamics of the reaction:



Compound	Standard molar entropy at 298 K, $S^\ominus / \text{J K}^{-1} \text{ mol}^{-1}$	Standard molar enthalpy of formation at 298 K, $\Delta_f H^\ominus / \text{kJ mol}^{-1}$	Colour
NO_2	+240.0	+33.2	brown
N_2O_4	+304.2		colourless

- (a) Calculate the entropy change for the reaction, using the information in the table. Include a sign and units in your answer.

(2)

- (b) Calculate the enthalpy change of formation, $\Delta_f H$, of N_2O_4 (g) at 298 K, using the information in the table and the enthalpy change of the reaction. Include a sign and units in your answer.

(2)

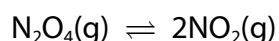
- (c) Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, at 298 K.
Give your answer to an appropriate number of significant figures.
Include a sign and units in your answer.

(3)

- (d) (i) Use your answers to parts (a) and (c) to calculate the total entropy change, ΔS_{total} , for this reaction at 298 K.

(1)

- (ii) This reaction can also be written as an equilibrium:



Calculate the temperature at which ΔS_{total} is zero for this equilibrium.

(2)

- (e) (i) Write the expression for the equilibrium constant, K_p , for this reaction, including the units, if any.

(2)

- (ii) In an experiment, 10 mol of $\text{N}_2\text{O}_4(\text{g})$ was placed in a closed container at 50°C . At equilibrium, 27% of the $\text{N}_2\text{O}_4(\text{g})$ had dissociated, and the pressure in the container was 4.0 atm.

Calculate the value of K_p at 50°C .

(4)

- (iii) The total pressure is doubled to 8.0 atm.
State the effect on K_p .

(1)

- (iv) The total pressure is doubled to 8.0 atm at constant temperature.
Explain the change in the percentage dissociation of $\text{N}_2\text{O}_4(\text{g})$ by considering the effect on the partial pressures of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$.

(3)

(Total for Question 23 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS