

Please check the examination details below before entering your candidate information

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Pearson Edexcel International Advanced Level

Time 1 hour 45 minutes

Paper reference **WCH14/01**

Chemistry

International Advanced Level

UNIT 4: Rates, Equilibria and Further Organic Chemistry

You must have:
Scientific calculator, Data Booklet, ruler

Total Marks

Instructions

- Use **black** ink or 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.*

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 the question 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.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Show all your working in calculations and include units where appropriate.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ►

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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 This question is about proton NMR spectroscopy.

(a) How many peaks are there in the **low** resolution proton NMR spectrum of 2-methylpropan-2-ol?

(1)

- ☐ A one
- ☐ B two
- ☐ C three
- ☐ D four

(b) Which compound has **three** peaks with relative peak areas of 3:2:1 in its **low** resolution proton NMR spectrum?

(1)

- ☐ A propanal
- ☐ B propane
- ☐ C propan-1-ol
- ☐ D propan-2-ol

(c) Which compound does **not** have a singlet peak in its **high** resolution proton NMR spectrum?

(1)

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

(Total for Question 1 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.



- 2 The high resolution mass spectrum of an organic compound **X** has a molecular ion peak with $m/z = 58.0417$ and another peak with $m/z = 29.0390$.

Which compound is **X**?

[A_r values: H = 1.0078 C = 12.0000 O = 15.9949]

- ☐ **A** CH_3COCH_3
- ☐ **B** $\text{CH}_3\text{CH}_2\text{CHO}$
- ☐ **C** $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- ☐ **D** $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$

(Total for Question 2 = 1 mark)

- 3 A high performance liquid chromatography (HPLC) system used a column with a non-polar stationary phase and a solvent of methanol and water.

A mixture of octane, octanal and octan-1-ol was placed into the HPLC column.

What is the order of retention times?

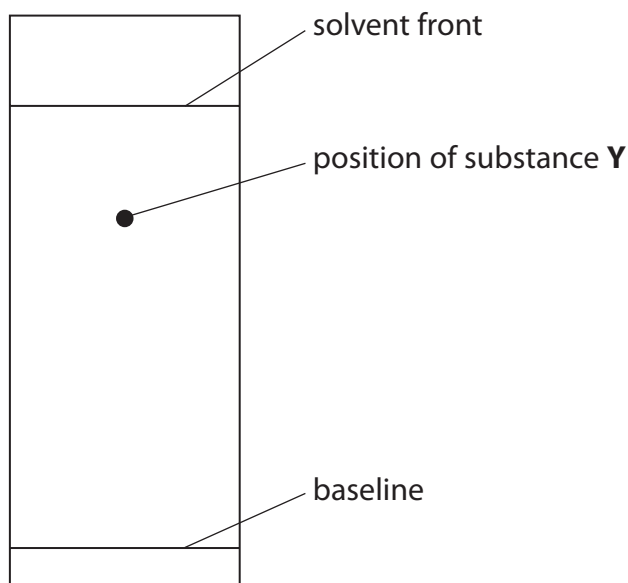
	Shortest retention time	Intermediate retention time	Longest retention time
<input type="checkbox"/> A	octane	octanal	octan-1-ol
<input type="checkbox"/> B	octanal	octan-1-ol	octane
<input type="checkbox"/> C	octane	octan-1-ol	octanal
<input type="checkbox"/> D	octan-1-ol	octanal	octane

(Total for Question 3 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.



- 4 A diagram of a thin layer chromatogram of substance **Y** is shown.



What is the R_f value of substance **Y**?

- ☐ A 0.25
- ☐ B 0.60
- ☐ C 0.75
- ☐ D 1.33

(Total for Question 4 = 1 mark)

- 5 Which reaction cannot form a carboxylic acid?

- ☐ A oxidation of primary alcohol
- ☐ B acidic hydrolysis of a nitrile
- ☐ C alkaline hydrolysis of an ester
- ☐ D acyl chloride reacting with water

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.



6 Which alcohol could **not** be formed by the reduction of an aldehyde or a ketone?

- ☐ A 2-methylpentan-1-ol
- ☐ B 3-methylpentan-2-ol
- ☐ C 3-methylpentan-3-ol
- ☐ D 2-methylpentan-3-ol

(Total for Question 6 = 1 mark)

7 What is the pH of a $0.010 \text{ mol dm}^{-3}$ aqueous solution of carbonic acid?

[K_a of carbonic acid = $4.5 \times 10^{-7} \text{ mol dm}^{-3}$ at 298 K]

- ☐ A 2.00
- ☐ B 4.17
- ☐ C 6.35
- ☐ D 8.35

(Total for Question 7 = 1 mark)

8 What is the pH of a 0.27 mol dm^{-3} aqueous solution of sodium hydroxide?

[$K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K]

- ☐ A 0.57
- ☐ B 13.43
- ☐ C 13.73
- ☐ D 14.57

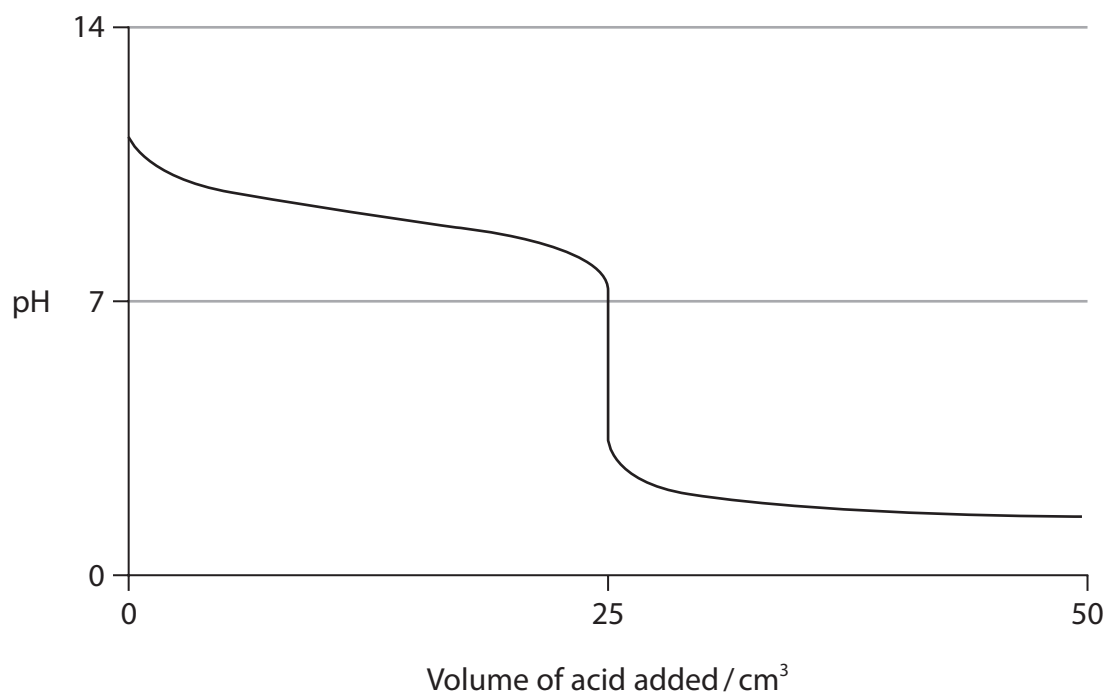
(Total for Question 8 = 1 mark)

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- 9 A 0.1 mol dm^{-3} aqueous acid solution was added to 25 cm^3 of a 0.1 mol dm^{-3} aqueous solution of an alkali.

The titration curve shown was obtained.



- (a) Which titration would produce this curve?

(1)

- ☐ A ethanoic acid added to sodium hydroxide
- ☐ B hydrochloric acid added to sodium hydroxide
- ☐ C ethanoic acid added to ammonia
- ☐ D hydrochloric acid added to ammonia

- (b) Which indicator would be **most** suitable for this titration?

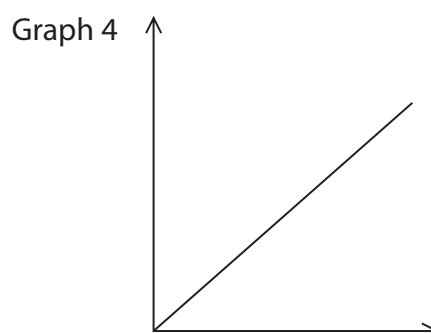
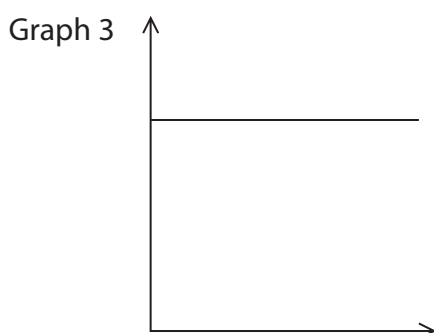
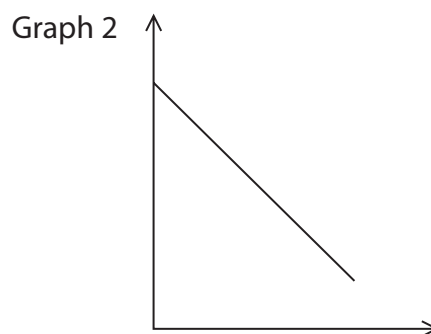
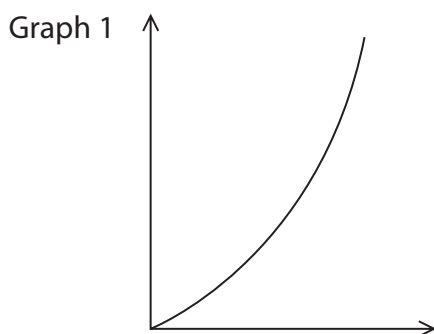
(1)

	Indicator	pH range
<input type="checkbox"/> A	malachite green	0.2–1.8
<input type="checkbox"/> B	methyl yellow	2.9–4.0
<input type="checkbox"/> C	methyl red	4.2–6.3
<input type="checkbox"/> D	thymol blue	8.0–9.6

(Total for Question 9 = 2 marks)



10 Four graphs are shown.



- (a) Which graph shows the rate of reaction on the vertical axis plotted against concentration of the reactant on the horizontal axis for a **zero** order reaction?

(1)

- ☐ **A** Graph 1
- ☐ **B** Graph 2
- ☐ **C** Graph 3
- ☐ **D** Graph 4

- (b) Which graph shows the rate of reaction on the vertical axis plotted against concentration of the reactant on the horizontal axis for a **first** order reaction?

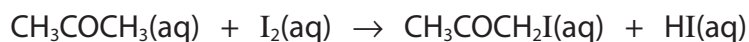
(1)

- ☐ **A** Graph 1
- ☐ **B** Graph 2
- ☐ **C** Graph 3
- ☐ **D** Graph 4

(Total for Question 10 = 2 marks)



11 Propanone reacts with iodine in the presence of a sulfuric acid catalyst.



(a) Which method would be most suitable for following this reaction?

(1)

- ☐ A colorimetry
- ☐ B timing how long the solution takes to go cloudy
- ☐ C quenching and titrating with an acid
- ☐ D quenching and titrating with starch solution

(b) The rate equation for this reaction is:

$$\text{rate} = k[\text{H}^+][\text{CH}_3\text{COCH}_3]$$

Two experiments were carried out. In both experiments the concentration of propanone and iodine remained the same but the concentration of the sulfuric acid was changed.

The initial rate in the first experiment was three times faster than the initial rate in the second experiment.

In the first experiment the initial pH was 1.50

What is the initial pH in the second experiment?

(1)

- ☐ A 1.02
- ☐ B 1.98
- ☐ C 2.28
- ☐ D 4.50

(Total for Question 11 = 2 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.



- 12** A series of experiments was carried out to determine the rate constant, k , of the reaction between bromate(V) ions and bromide ions at different temperatures, T .

A graph of $\ln k$ was plotted against $\frac{1}{T}$. The gradient of the line was -4670 K .

The Arrhenius equation may be written as

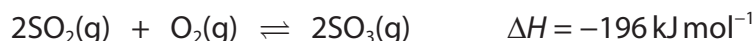
$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \quad R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

What is the activation energy of this reaction?

- ☐ **A** $+38.8 \text{ kJ mol}^{-1}$
- ☐ **B** $+38.8 \text{ J mol}^{-1} \text{ K}^{-1}$
- ☐ **C** $+562 \text{ J mol}^{-1}$
- ☐ **D** $+562 \text{ J mol}^{-1} \text{ K}^{-1}$

(Total for Question 12 = 1 mark)

- 13** Solid vanadium(V) oxide catalyses the equilibrium shown.



Which statement is correct?

- ☐ **A** vanadium(V) oxide is a homogeneous catalyst
- ☐ **B** decreasing the pressure would increase the equilibrium yield of sulfur trioxide
- ☐ **C** increasing the surface area of the catalyst would increase the equilibrium yield of sulfur trioxide
- ☐ **D** decreasing the temperature would increase the equilibrium yield of sulfur trioxide

(Total for Question 13 = 1 mark)

- 14** In which series does the standard molar entropy of the compounds **increase**?

- ☐ **A** $\text{CaO(s)} < \text{H}_2\text{O(l)} < \text{CO}_2(\text{g}) < \text{SO}_2(\text{g})$
- ☐ **B** $\text{CaO(s)} < \text{H}_2\text{O(l)} < \text{SO}_2(\text{g}) < \text{CO}_2(\text{g})$
- ☐ **C** $\text{SO}_2(\text{g}) < \text{CO}_2(\text{g}) < \text{H}_2\text{O(l)} < \text{CaO(s)}$
- ☐ **D** $\text{CO}_2(\text{g}) < \text{SO}_2(\text{g}) < \text{H}_2\text{O(l)} < \text{CaO(s)}$

(Total for Question 14 = 1 mark)



15 Experimental lattice energy values determined using the Born-Haber cycle often differ from calculated theoretical values.

The ionic radii and charges of some ions are shown.

P, Q, R and S are **not** the chemical symbols of the elements.

Ion	Ionic radius / nm
P⁺	0.076
Q⁺	0.167
R⁻	0.133
S⁻	0.220

Which of these compounds would be expected to show the largest percentage difference between the experimental and theoretical lattice energies?

- ☐ **A PR**
- ☐ **B PS**
- ☐ **C QR**
- ☐ **D QS**

(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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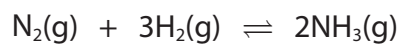


SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

16 This question is about ammonia and ammonium chloride.

(a) Ammonia is produced by reacting nitrogen and hydrogen as shown.



(i) Write the expression for the equilibrium constant, K_p .

(1)

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- (ii) An equilibrium was established by mixing nitrogen and hydrogen in a 1:3 ratio by volume, at a temperature of 450°C and pressure of 200 atm. The equilibrium mixture contained 28% of ammonia by volume.

Complete the table.

(3)

Substance	Mole fraction	Partial pressure / atm
N_2		
H_2		
NH_3	0.28	56

- (iii) Calculate the equilibrium constant.

Give your answer to an appropriate number of significant figures and include units, if required.

(3)

- (iv) When the temperature was reduced to 400°C at the same pressure, the equilibrium mixture contained 36% of ammonia.

Explain what can be deduced about this reaction from this information.

(2)

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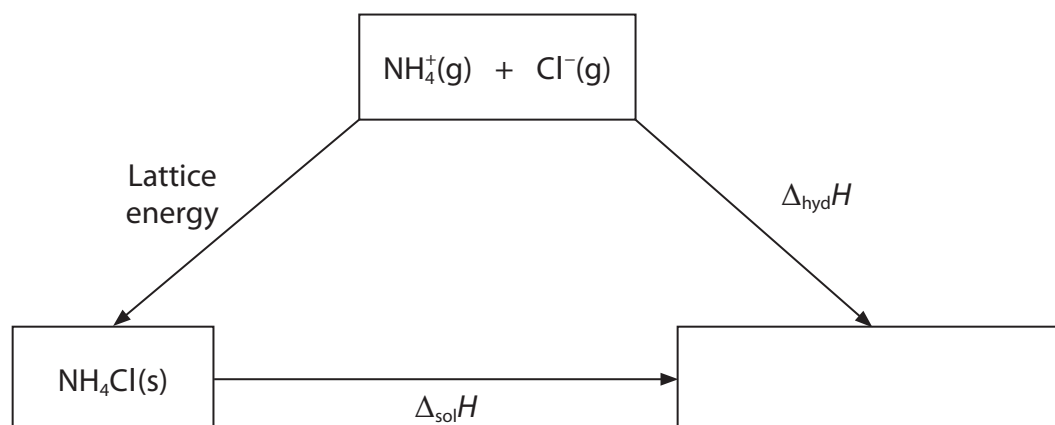
- (b) Ammonium chloride can be produced by reacting ammonia with hydrogen chloride.

Ammonium chloride is a white solid that is very soluble in water.

Hess's Law can be used to calculate the enthalpy of solution of ammonium chloride, using hydration enthalpies and lattice energy.

- (i) Complete the Hess cycle by filling in the empty box.

(1)



- (ii) Complete the expression for the enthalpy change of solution using the hydration enthalpies and lattice energy.

(1)

$$\Delta_{\text{sol}}H =$$

- (iii) Calculate the enthalpy change of solution, using your expression in (b)(ii) and these data.

Enthalpy change of hydration of $\text{NH}_4^+ = -307 \text{ kJ mol}^{-1}$

Enthalpy change of hydration of $\text{Cl}^- = -378 \text{ kJ mol}^{-1}$

Lattice energy of $\text{NH}_4\text{Cl} = -705 \text{ kJ mol}^{-1}$

(2)



- (iv) A student suggested that the enthalpy change of solution of ammonium bromide would be of a similar magnitude to the enthalpy change of solution of ammonium chloride.

Comment on this suggestion in terms of the hydration enthalpies and lattice energies of these two compounds.

(3)

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- (c) Write an **ionic** equation to show why aqueous solutions of ammonium chloride are acidic. State symbols are not required.

(1)

(Total for Question 16 = 17 marks)



17 This question is about carbonyl compounds.

- (a) Three carbonyl compounds, **A**, **B** and **C**, are **straight-chain** structural isomers, with the formula $C_5H_{10}O$.
Only isomer **A** reacts with Tollens' reagent to give a silver mirror.
Only isomer **B** reacts with iodine in the presence of alkali to produce pale yellow crystals.

Draw the **displayed** structures of these three isomers.

(3)

A	
B	
C	

- (b) Another carbonyl compound, propanal, reacts with HCN in the presence of KCN to form a racemic mixture of two optical isomers of $CH_3CH_2CH(OH)CN$.

(i) Give the IUPAC name for $CH_3CH_2CH(OH)CN$.

(1)

(ii) Describe how you could distinguish between pure samples of the two optical isomers.

(1)



P 7 0 9 6 7 A 0 1 5 3 2

(iii) Explain, with reference to the reaction mechanism, why this reaction produces a racemic mixture.

(2)

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(c) (i) Propanone, an isomer of propanal, also reacts with HCN in the presence of KCN.

Draw the **skeletal** formula of the product of this reaction.

(1)

(ii) State why the product formed in (c)(i) does **not** show optical isomerism.

(1)

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(d) ^{13}C NMR spectroscopy provides information about the structures of propanal and propanone.

- (i) Identify the chemical shift range and carbon environment of **one** peak you would expect to see in **both** spectra.

(1)

Chemical shift range	Carbon environment

- (ii) State the number of peaks you would expect to see in each ^{13}C NMR spectrum.

(1)

Propanal

Propanone

(Total for Question 17 = 11 marks)

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***18** Compare and contrast the reactions of ethanoyl chloride with water, with ethanol and with ammonia.

Refer to the structural features of the molecules that determine the type of reaction. Identify the products of the reactions. You may include equations in your answers.

(6)

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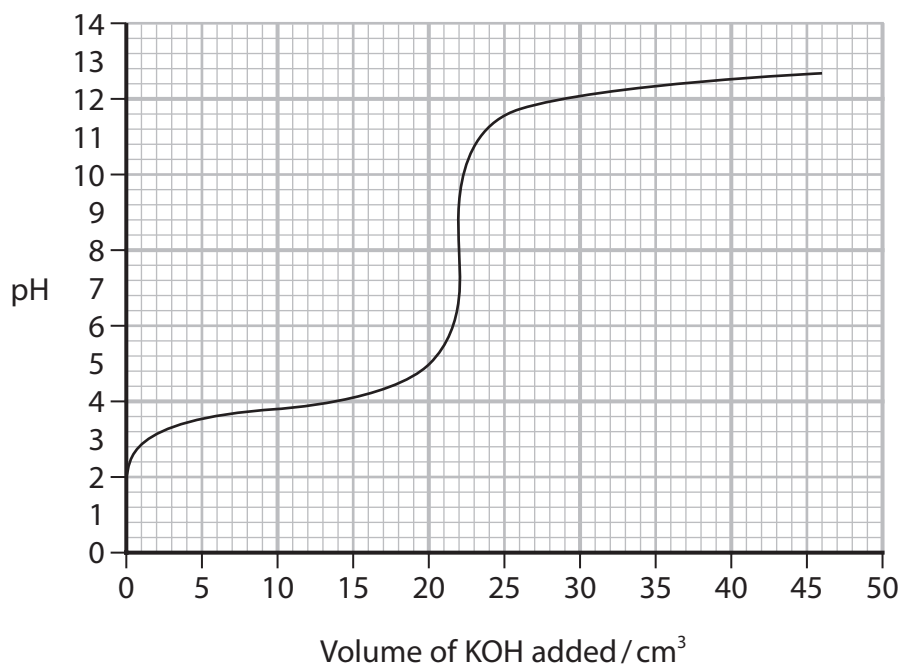
(Total for Question 18 = 6 marks)



19 This question is about methanoic acid and propanoic acid.

- (a) A student carried out a titration to find the concentration of an aqueous solution of potassium hydroxide.

25.00 cm^3 of 0.150 mol dm^{-3} aqueous methanoic acid was pipetted into a conical flask. Potassium hydroxide was added from a burette while measuring the pH. The titration curve is shown.



- (i) Complete the equation for the reaction taking place in this titration. State symbols are not required.

(1)



- (ii) Calculate the concentration of the potassium hydroxide solution, using your equation in (i) and the titration curve.

(2)

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- (iii) Use the titration curve to determine a value for the acid dissociation constant, K_a , of methanoic acid.

(3)

- (b) A student prepared a buffer by mixing together equimolar aqueous solutions of propanoic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, and sodium propanoate, $\text{CH}_3\text{CH}_2\text{COONa}$.

The acid dissociation constant, K_a , for propanoic acid is $1.3 \times 10^{-5} \text{ mol dm}^{-3}$.

Calculate the volume ratio of propanoic acid to sodium propanoate needed to produce a buffer solution with a pH of 4.6

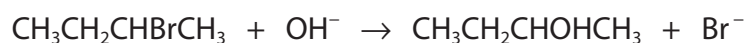
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(Total for Question 19 = 8 marks)



20 This question is about the hydrolysis of 2-bromobutane with aqueous sodium hydroxide at 298 K.

The equation for the reaction is:



- (a) The data shown were obtained in an experiment to investigate the kinetics of this reaction.

Experiment number	Initial concentration / mol dm^{-3}		Initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
	$[\text{CH}_3\text{CH}_2\text{CHBrCH}_3]$	$[\text{OH}^-]$	
1	0.100	0.100	1.01×10^{-3}
2	0.200	0.100	2.02×10^{-3}
3	0.100	0.200	1.01×10^{-3}

- (i) Deduce the order of reaction with respect to 2-bromobutane and with respect to hydroxide ions. Justify your answers.

(2)

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- (ii) Write the rate equation for the reaction using your answer to (a)(i).

(1)



- (iii) Calculate the rate constant for Experiment 1.
Include units in your answer.

(2)

- (b) Draw the mechanism for this reaction that is consistent with your rate equation.
Include curly arrows, and any relevant dipoles and lone pairs of electrons.

(3)

(Total for Question 20 = 8 marks)

TOTAL FOR SECTION B = 50 MARKS

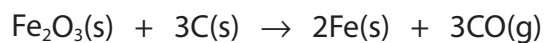


SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

21 This question is about oxides of iron.

(a) The equation for the reduction of iron(III) oxide by carbon is shown.



Some data relating to this reaction are shown.

Substance	Fe_2O_3	C	Fe	CO
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-824.2	0	0	-110.5
$S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$	87.4	5.7	27.3	197.6

(i) Calculate the standard enthalpy change, $\Delta_r H^\ominus$, for the reduction of iron(III) oxide by carbon.

(2)

(ii) Calculate the entropy change, ΔS_{system} , for this reaction.

(3)

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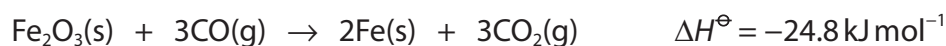
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- (iii) Calculate the temperature at which this reaction becomes feasible, using your answers from (a)(i) and (a)(ii).

(3)

- (b) The equation for the reduction of iron(III) oxide by carbon monoxide is shown.



The entropy change, $\Delta S_{\text{system}}^\ominus$, for this reaction is $+15.2 \text{ J mol}^{-1} \text{ K}^{-1}$.

- (i) Explain why the reaction should be feasible at any temperature.

(2)

- (ii) Explain how an increase in temperature would affect $\Delta S_{\text{total}}^\ominus$ of this reaction.
No calculation is required.

(3)



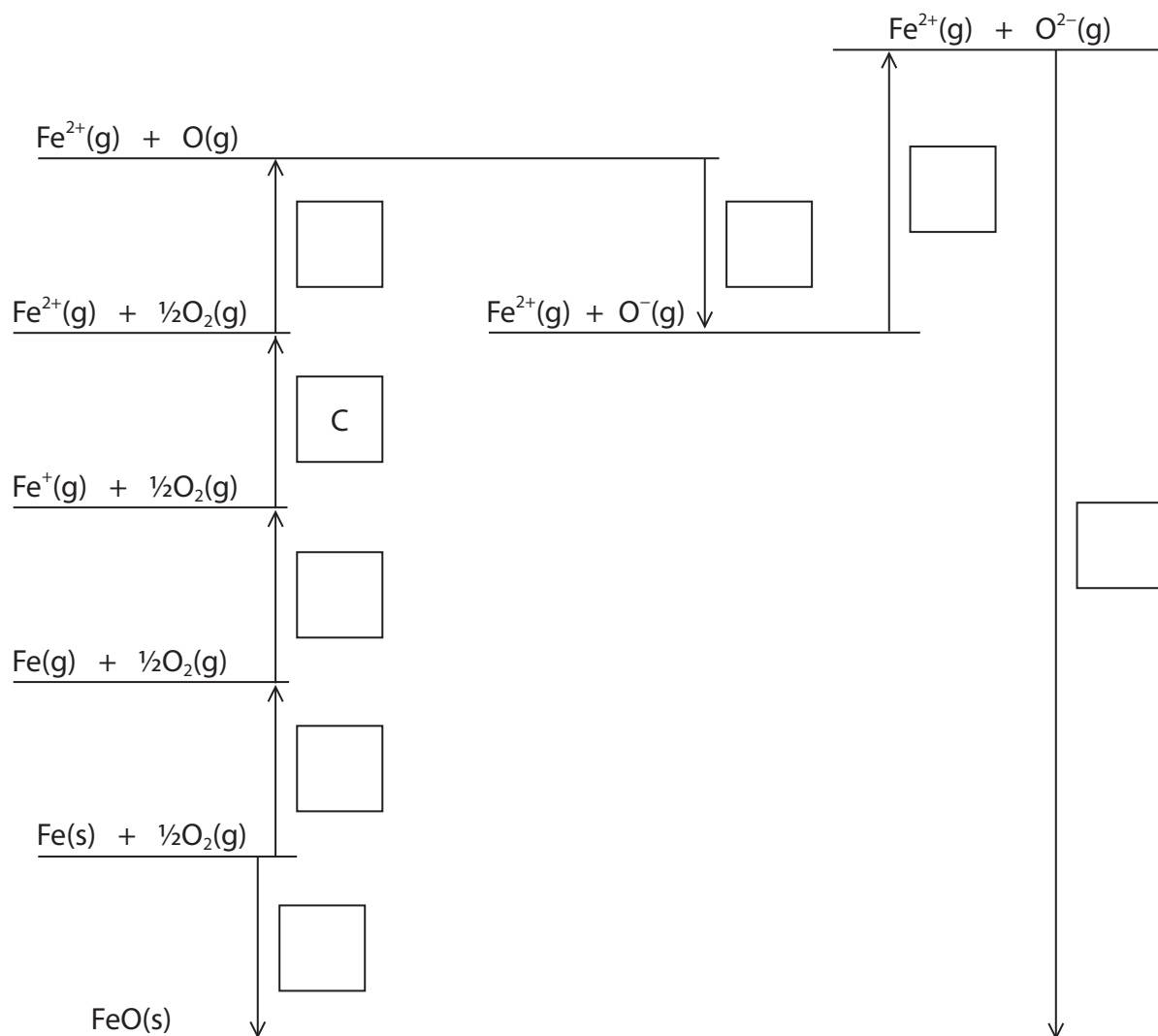
- (c) Iron also forms iron(II) oxide. The data in the table can be used to construct a Born-Haber cycle for iron(II) oxide, FeO.

Letter	Enthalpy change	Value / kJ mol^{-1}
A	Enthalpy change of atomisation of iron	+416
B	First ionisation energy of iron	+759
C	Second ionisation energy of iron	
D	Enthalpy change of formation of iron(II) oxide	-272
E	First electron affinity of oxygen	-141
F	Second electron affinity of oxygen	+798
G	Lattice energy of iron(II) oxide	-3920
H	Enthalpy change of atomisation of oxygen ($\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$)	+249



- (i) Complete the Born-Haber cycle by putting letters in the boxes to label the energy changes.

(3)



- (ii) Calculate the value for second ionisation energy of iron, C.

(2)



(iii) Suggest why the second electron affinity of oxygen is positive.

(2)

(Total for Question 21 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS

TOTAL FOR PAPER = 90 MARKS

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