

Please check the examination details below before entering your candidate information

Candidate surname

Other names

**Pearson Edexcel**  
**International**  
**Advanced Level**

Centre Number

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Candidate Number

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**Tuesday 2 June 2020**

Afternoon (Time: 1 hour 45 minutes)

Paper Reference **WCH14/01**

**Chemistry**

**International Advanced Level**

**Unit 4: Rates, Equilibria and Further Organic Chemistry**

**Candidates must have: Scientific calculator**  
**Data Booklet**  
**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.*

### 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 your working in calculations and include units where appropriate.
- Check your answers if you have time at the end.

Turn over ►

## SECTION A

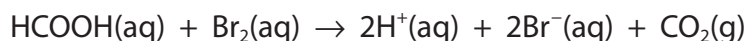
Answer ALL the questions in this section.

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 ☐. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☐.

- 1 Bromine oxidises methanoic acid to carbon dioxide.

The equation for the reaction is



Which of the following methods would **not** be suitable for measuring the progress of this reaction?

- ☐ A colorimetry
- ☐ B measuring electrical conductivity
- ☐ C quenching and titrating with acid
- ☐ D measuring the volume of gas

(Total for Question 1 = 1 mark)

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- 2 The rate of the reaction between two compounds, **Y** and **Z**, was investigated. The results are shown.

| Experiment | Initial concentration of <b>Y</b><br>/ mol dm <sup>-3</sup> | Initial concentration of <b>Z</b><br>/ mol dm <sup>-3</sup> | Initial rate<br>/ mol dm <sup>-3</sup> s <sup>-1</sup> |
|------------|-------------------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------|
| 1          | 0.64                                                        | 0.24                                                        | $8.00 \times 10^{-3}$                                  |
| 2          | 0.64                                                        | 0.48                                                        | $3.20 \times 10^{-2}$                                  |
| 3          | 0.32                                                        | 0.48                                                        | $3.20 \times 10^{-2}$                                  |

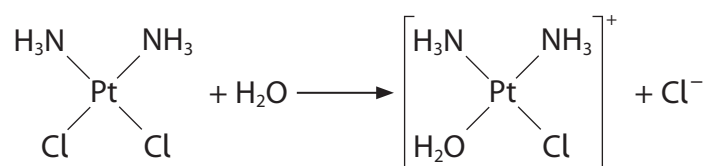
What are the orders of reaction with respect to **Y** and **Z**?

|                                   | Order with respect to <b>Y</b> | Order with respect to <b>Z</b> |
|-----------------------------------|--------------------------------|--------------------------------|
| <input type="checkbox"/> <b>A</b> | 0                              | 1                              |
| <input type="checkbox"/> <b>B</b> | 0                              | 2                              |
| <input type="checkbox"/> <b>C</b> | 1                              | 1                              |
| <input type="checkbox"/> <b>D</b> | 1                              | 2                              |

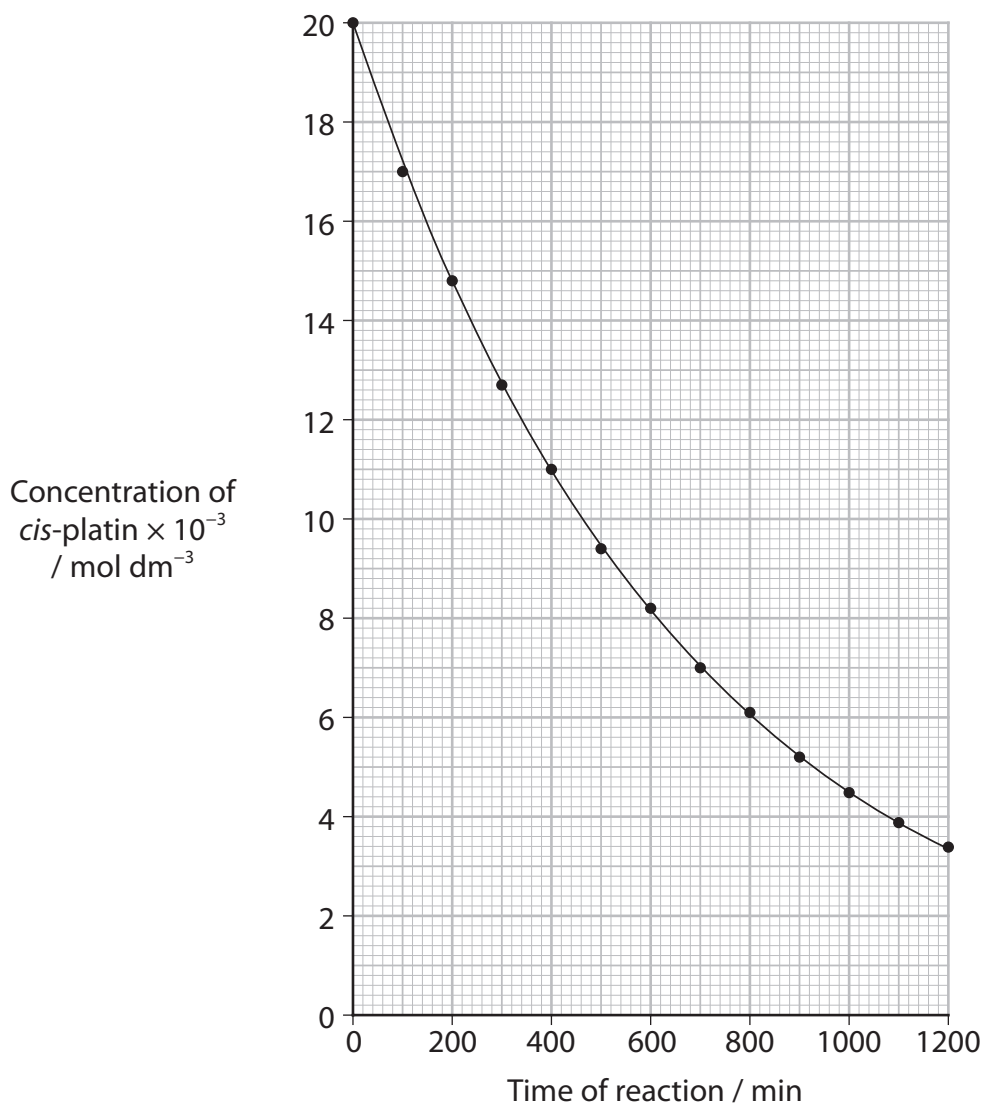
(Total for Question 2 = 1 mark)

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- 3 The inorganic anti-cancer drug *cis*-platin,  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ , is hydrolysed by water to make it active. The reaction is



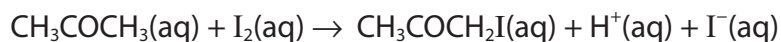
The hydrolysis is first order overall. The half-life can be found from a graph of the concentration of *cis*-platin against time.



The half-life of the reaction is

- ☐ A 430 min
- ☐ B 460 min
- ☐ C 590 min
- ☐ D 600 min

4 Propanone reacts with iodine in acidic solution.



The rate equation for the formation of iodopropanone is found to be

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

(a) Which of the following is true?

(1)

- ☐ A the units for the rate constant are  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
- ☐ B the reaction is a first order reaction overall
- ☐ C the units for the rate are  $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
- ☐ D doubling the concentrations of propanone and of iodine quadruples the rate

(b) Which of the following is **not** true?

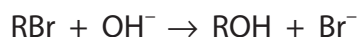
(1)

- ☐ A the reaction rate increases if the temperature is raised
- ☐ B the rate constant increases if the temperature is raised
- ☐ C the addition of a small amount of sodium hydroxide decreases the reaction rate
- ☐ D the rate is unchanged when the hydrogen ion concentration is doubled

(Total for Question 4 = 2 marks)

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- 5 The equation shows the hydrolysis of a bromoalkane.



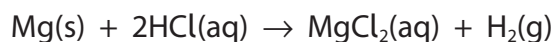
The rate equation is  $\text{rate} = k[\text{RBr}]$

RBr is most likely to be

- ☐ A bromomethane
- ☐ B 2-bromopropane
- ☐ C 1-bromo-2-methylpropane
- ☐ D 2-bromo-2-methylpropane

(Total for Question 5 = 1 mark)

- 6 The equation for an exothermic reaction is shown.



Which of these is true?

- ☐ A  $\Delta H$  is positive
- ☐ B  $\Delta S_{\text{surroundings}}$  is positive
- ☐ C  $\Delta S_{\text{system}}$  is negative
- ☐ D  $\Delta S_{\text{total}}$  is negative

(Total for Question 6 = 1 mark)

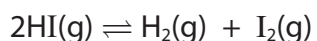
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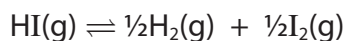
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- 7 The equation for the equilibrium decomposition of hydrogen iodide into hydrogen and iodine can be written in two ways.



Equilibrium constant =  $K_c$

or



Equilibrium constant =  $K'_c$

What is the expression linking the two equilibrium constants?

- ☐ A  $K_c = (K'_c)^2$
- ☐ B  $K_c = K'_c$
- ☐ C  $K_c = 2(K'_c)$
- ☐ D  $K_c = \sqrt{K'_c}$

(Total for Question 7 = 1 mark)

- 8 A buffer solution contains ethanoic acid, with a concentration of  $0.10 \text{ mol dm}^{-3}$ , and sodium ethanoate, with a concentration of  $0.050 \text{ mol dm}^{-3}$ .

$K_a$  for ethanoic acid =  $1.7 \times 10^{-5} \text{ mol dm}^{-3}$

The pH of this buffer solution is

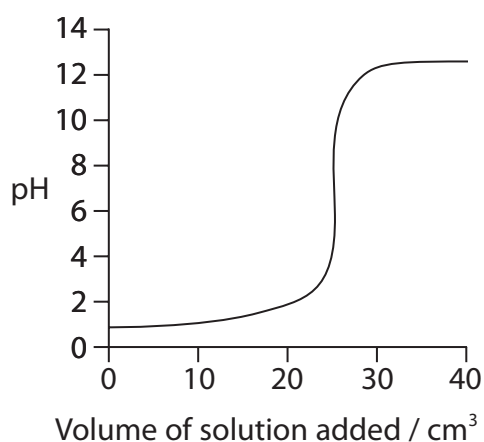
- ☐ A 2.88
- ☐ B 4.47
- ☐ C 4.77
- ☐ D 5.07

(Total for Question 8 = 1 mark)

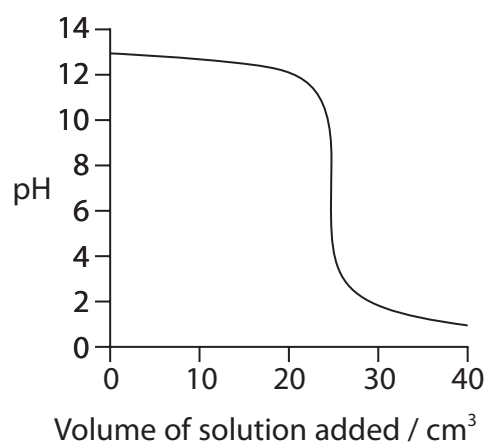
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- 9 The graphs show the changes in pH during a series of titrations.  
Each titration involves two solutions, each of concentration  $0.1 \text{ mol dm}^{-3}$ .

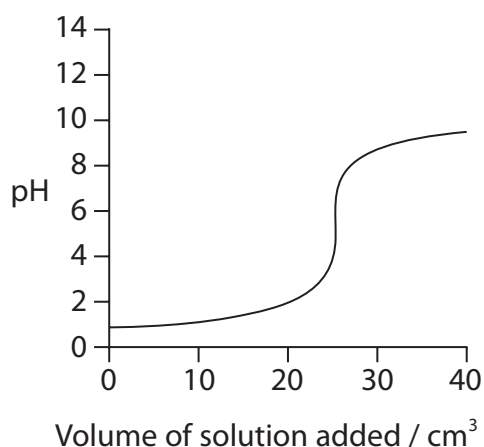
Graph 1



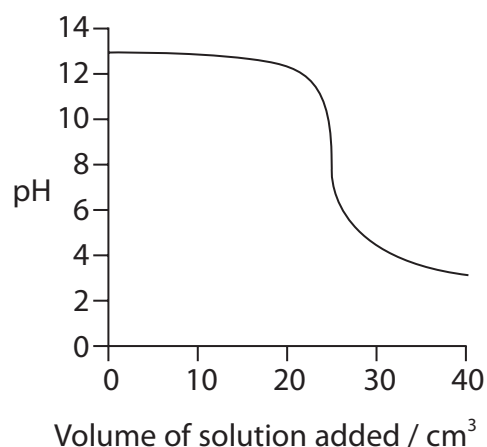
Graph 2



Graph 3



Graph 4



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- (a) Which graph has ethanoic acid as one of the reactants?

(1)

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

(b) Which graph shows a solution that has an acidic pH at the end-point?

(1)

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

(c) Which indicator is suitable for the titration shown in Graph 3?  
Use your Data Booklet.

(1)

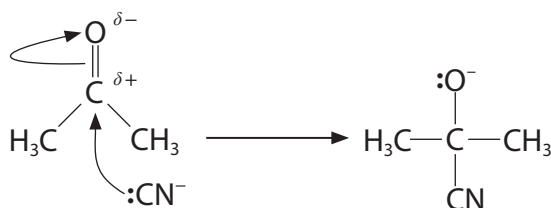
- ☐ A bromocresol green
- ☐ B bromothymol blue
- ☐ C phenol red
- ☐ D thymol blue (acid)

(Total for Question 9 = 3 marks)

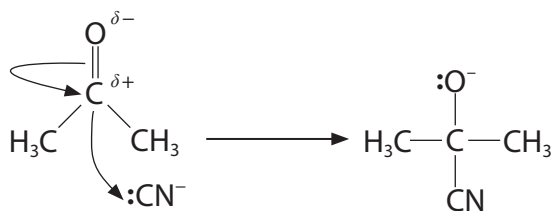
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10 Which diagram shows the first step of the mechanism for the nucleophilic addition of hydrogen cyanide to propanone in the presence of potassium cyanide?

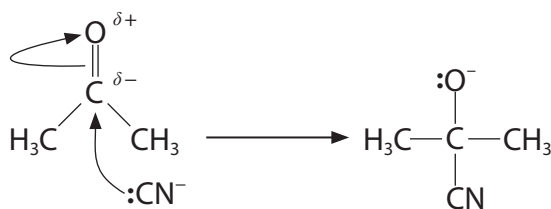
☐ A



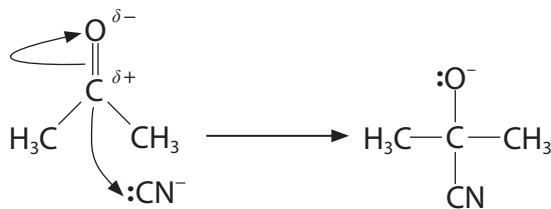
☐ B



☐ C



☐ D



(Total for Question 10 = 1 mark)

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11 When propanone reacts with iodine in the presence of sodium hydroxide, the precipitate formed has the formula

- ☐ A  $\text{CH}_3\text{I}$
- ☐ B  $\text{CHI}_3$
- ☐ C  $\text{CH}_3\text{COCH}_2\text{I}$
- ☐ D  $\text{CH}_3\text{COCl}_3$

(Total for Question 11 = 1 mark)

12 Which of the following could **not** be formed when methylamine is added to ethanoyl chloride?

- ☐ A  $\text{HCl}$
- ☐ B  $\text{CH}_3\text{NH}_3^+\text{Cl}^-$
- ☐ C  $\text{CH}_3\text{CONH}_2$
- ☐ D  $\text{CH}_3\text{CONHCH}_3$

(Total for Question 12 = 1 mark)

13 In which of these esters is the percentage by mass of carbon 54.5 %?

- ☐ A methyl methanoate,  $\text{HCOOCH}_3$
- ☐ B methyl ethanoate,  $\text{CH}_3\text{COOCH}_3$
- ☐ C ethyl ethanoate,  $\text{CH}_3\text{COOCH}_2\text{CH}_3$
- ☐ D ethyl methanoate,  $\text{HCOOCH}_2\text{CH}_3$

(Total for Question 13 = 1 mark)

14 An organic compound that reacts with **both** lithium tetrahydridoaluminate(III) (lithium aluminium hydride) **and** magnesium could be

- ☐ A an aldehyde
- ☐ B a carboxylic acid
- ☐ C a ketone
- ☐ D a tertiary alcohol

(Total for Question 14 = 1 mark)

15 The following methods can be used to distinguish between pairs of organic compounds with **no** further tests.

- A warm each compound with Fehling's or Benedict's solution
- B warm each compound with acidified potassium dichromate(VI) solution
- C add 2,4-dinitrophenylhydrazine (Brady's reagent) to each compound
- D add a few drops of each compound, drop by drop, to water

(a) Which test would distinguish between 2-methylpropan-2-ol,  $(\text{CH}_3)_3\text{COH}$ , and butanone,  $\text{CH}_3\text{CH}_2\text{COCH}_3$ ?

(1)

- ☐ A
- ☐ B
- ☐ C
- ☐ D

(b) Which test would distinguish between 2-methylpropan-2-ol,  $(\text{CH}_3)_3\text{COH}$ , and butan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ?

(1)

- ☐ A
- ☐ B
- ☐ C
- ☐ D

(c) Which test could **not** be used to distinguish between 2-methylpropan-2-ol,  $(\text{CH}_3)_3\text{COH}$ , and butanal,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ ?

(1)

- ☐ A
- ☐ B
- ☐ C
- ☐ D

(Total for Question 15 = 3 marks)

TOTAL FOR SECTION A = 20 MARKS

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## SECTION B

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

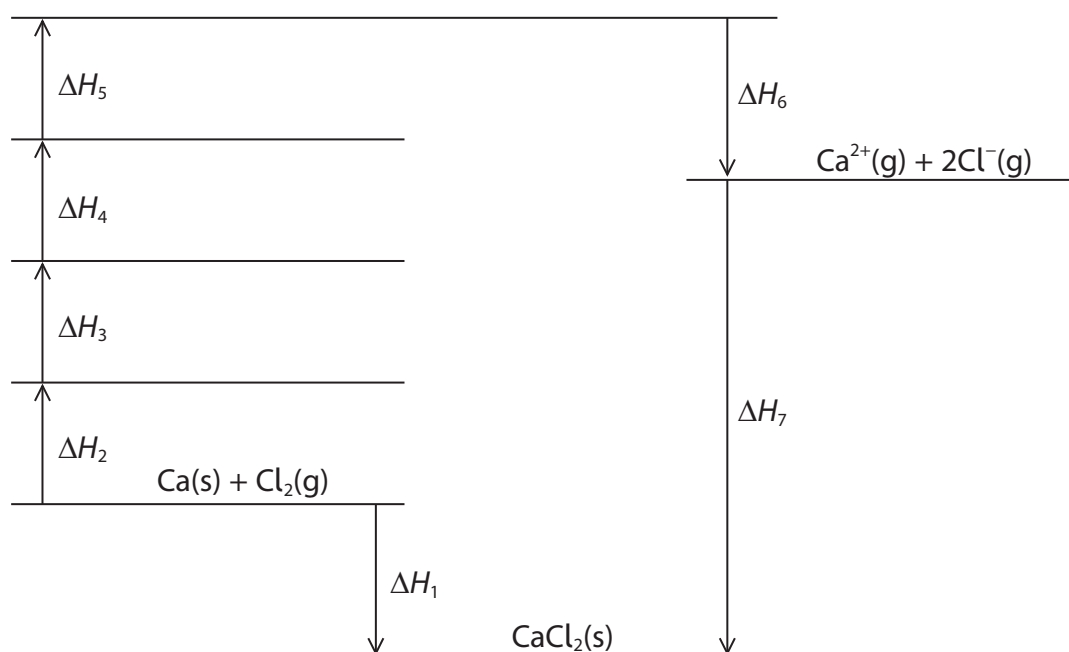
16 This question concerns calcium chloride,  $\text{CaCl}_2$ .

(a) Some energy changes related to calcium chloride are shown.

| Energy change                                             | Value / $\text{kJ mol}^{-1}$ |
|-----------------------------------------------------------|------------------------------|
| Atomisation energy of calcium                             | +178.2                       |
| Atomisation energy of chlorine                            | +121.7                       |
| Electron affinity of chlorine                             | -348.8                       |
| First ionisation energy of calcium                        | +590.0                       |
| Standard enthalpy change of formation of calcium chloride | -795.8                       |
| Experimental lattice energy of calcium chloride           | -2 258                       |
| Second ionisation energy of calcium                       | To be calculated             |

(i) Complete the Born-Haber cycle by writing appropriate chemical formulae on the horizontal lines. Include state symbols and relevant electrons.

(4)



- (ii) Calculate the second ionisation energy of calcium using the cycle and the values given in the table. Include a sign and units with your value.

(3)

- (b) The theoretical lattice energy of formation of  $\text{CaCl}_2$  is  $-2223 \text{ kJ mol}^{-1}$ .  
Explain why the experimental lattice energy of  $\text{CaCl}_2$  is more exothermic than the theoretical value.

(3)

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(c) The table shows the theoretical lattice energies of some chlorides of Group 2.

| Group 2 metal chloride                | magnesium chloride | calcium chloride | strontium chloride | barium chloride |
|---------------------------------------|--------------------|------------------|--------------------|-----------------|
| Lattice energy / $\text{kJ mol}^{-1}$ | -2326              | -2223            | -2127              | -2033           |

Explain the trend in **theoretical** lattice energies on descending Group 2.

(3)

(d) Calculate the enthalpy change of solution of calcium chloride,  $\text{CaCl}_2$ .

**Data**

$$\Delta_{\text{hyd}} H^{\ominus} (\text{Ca}^{2+}) = -1\,650 \text{ kJ mol}^{-1} \quad \Delta_{\text{hyd}} H^{\ominus} (\text{Cl}^{-}) = -364 \text{ kJ mol}^{-1}$$

$$\text{Experimental lattice energy } (\text{CaCl}_2) = -2\,258 \text{ kJ mol}^{-1}$$

(2)

(Total for Question 16 = 15 marks)

17 This question concerns six isomers each with the molecular formula  $C_5H_{10}O_2$ .

- (a) Isomers **A**, **B**, **C** and **D** are structural isomers that all react with aqueous sodium carbonate to produce carbon dioxide.

Isomer **A** is a straight-chain compound.

Isomer **B** has only two peaks in its high resolution proton NMR spectrum, both of which are singlets.

Isomer **C** contains a chiral centre but isomer **D** does not.

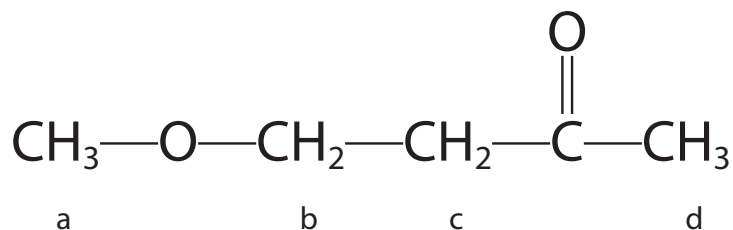
Give the structures of these **four** isomers.

(4)

| A | B |
|---|---|
|   |   |

| C | D |
|---|---|
|   |   |

- (b) (i) Isomer **E** contains an ether functional group (R-O-R) and a ketone functional group. The **low** resolution proton NMR spectrum of isomer **E** has four peaks. The displayed formula of isomer **E** is



The four hydrogen environments responsible for the four peaks are labelled. Complete the table of information regarding these peaks including the splitting pattern in the **high** resolution spectrum.

(3)

| Peak                                 | a         | b | c | d |
|--------------------------------------|-----------|---|---|---|
| Relative peak area                   | 3         |   |   |   |
| Chemical shift range, $\delta$ / ppm | 2.9 – 4.2 |   |   |   |
| Splitting                            | singlet   |   |   |   |

- (ii) State the number of peaks in the carbon-13 ( $^{13}\text{C}$ ) NMR spectrum of **E**.

(1)

(c) Isomer **F** is a neutral compound that smells of pears.

It can be formed by the reaction between compounds **V** and **W** in the presence of concentrated sulfuric acid.

Compound **V** has an absorption in its infrared spectrum at  $1720\text{ cm}^{-1}$  and a broad absorption around  $3050\text{ cm}^{-1}$ .

Compound **W** can be formed directly from propanal.

(i) Identify, by name or formula, compounds **V**, **W** and **F**.

Justify your answer by using **all** the available information.

(4)

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(ii) State the conditions required and the reagent needed to form compound **W** from propanal.

(1)

(iii) State the role of sulfuric acid in the formation of **F**.

(1)

(d) State which one of the isomers **A**, **E** and **F** has the highest boiling temperature. Justify your answer.

(3)

(Total for Question 17 = 17 marks)

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**18** This question concerns acidic solutions.

- (a) (i) A solution of hydrochloric acid has a pH of 1.125.

Calculate the concentration of hydrogen ions and of hydroxide ions, in  $\text{mol dm}^{-3}$ , in this solution.

$$[K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}]$$

(2)

- (ii) Calculate the volume of water which must be added to  $25.0 \text{ cm}^3$  of this solution to increase the pH from 1.125 to 1.500, giving your answer to an appropriate number of significant figures.

(4)

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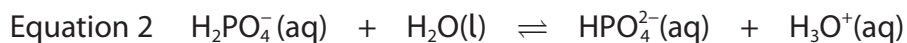
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- (b) Phosphoric(V) acid,  $\text{H}_3\text{PO}_4$ , is a weak acid, which dissolves in water, giving the equilibrium



The  $\text{H}_2\text{PO}_4^-$  ion formed when phosphoric(V) acid is added to water can dissociate further into  $\text{HPO}_4^{2-}$ .



.....

- (i) Identify the acids and bases in the spaces below Equation 2, linking the acid-base conjugate pairs. (2)
- (ii) Explain why very little dissociation of the  $\text{H}_2\text{PO}_4^-$  ion occurs in solutions of phosphoric(V) acid. (2)

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- (c) (i) Using Equation 1, write an expression for the acid dissociation constant,  $K_{a1}$ , for phosphoric(V) acid,  $H_3PO_4$ .

(1)

- (ii) A  $0.500 \text{ mol dm}^{-3}$  solution of phosphoric(V) acid has a pH of 1.20. Calculate the value of  $K_{a1}$ , stating its units.

Assume that there is no further dissociation of the  $H_2PO_4^-$  ion.

(4)

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- (d) Phosphate buffer solutions containing hydrogenphosphate ions,  $\text{HPO}_4^{2-}$ , and dihydrogenphosphate ions,  $\text{H}_2\text{PO}_4^-$ , are commonly used in biological research.

Explain, using a relevant ionic equation, how a solution containing these ions can act as a buffer when a small amount of **alkali** is added.

(3)

(Total for Question 18 = 18 marks)

TOTAL FOR SECTION B = 50 MARKS

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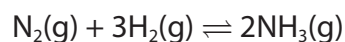
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## SECTION C

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

19 Ammonia is manufactured in the Haber Process.



In this process, pressures between 100 atm and 300 atm and temperatures between 675 K and 725 K are usually used.

- (a) (i) Calculate  $\Delta S_{\text{system}}^\ominus$  for this reaction at 298 K.  
Include a sign and units with your answer.

[Standard molar entropy,  $S^\ominus$ , for 1 mol of each gas, in  $\text{J K}^{-1} \text{mol}^{-1}$ :

$\text{N}_2 = 191.6$   $\text{H}_2 = 130.6$   $\text{NH}_3 = 192.3$ ]

(2)

- (ii) Explain, using ideas about disorder, whether the sign of your answer to (a)(i) is as expected.

(2)

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(iii) At 700 K, the enthalpy change for this reaction is  $\Delta H = -110.2 \text{ kJ mol}^{-1}$ .

Calculate the entropy change of the surroundings,  $\Delta S_{\text{surroundings}}$ , at 700 K.  
Include a sign and units in your answer.

(2)

(iv) At 700 K, the total entropy change,  $\Delta S_{\text{total}} = -78.7 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Calculate  $\Delta S_{\text{system}}$  for this reaction at 700 K.  
Include a sign and units in your answer.

(1)

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- \*(v) Explain **one** advantage and **one** disadvantage of using a temperature higher than 700 K in the Haber process.

Consider the effect of an increase in temperature on the rate of reaction, on the values of  $\Delta S_{\text{surroundings}}$  and  $\Delta S_{\text{total}}$  and on the equilibrium constant.

(6)

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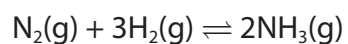
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- (b) (i) Write the expression for the equilibrium constant,  $K_p$ , for the reaction in the Haber Process.



(1)

- (ii) A mixture of nitrogen, hydrogen and ammonia is at equilibrium at 255 atm and 700 K. The partial pressure of nitrogen is 25 atm and that of hydrogen is 150 atm.

Calculate the equilibrium constant,  $K_p$ , for the formation of ammonia, at 700 K. Include units in your answer.

(3)

(iii) The pressure of the system is doubled at constant temperature.

Explain the effect of this on the yield of ammonia by considering the change in the  $K_p$  expression and hence the position of equilibrium.

(3)

(Total for Question 19 = 20 marks)

**TOTAL FOR SECTION C = 20 MARKS**

**TOTAL FOR PAPER = 90 MARKS**

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